IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

In re Application of:	)
	)
HOLMES et al.	) Group Art Unit: 1711
	)
Application No.: 09/529,873	) Examiner: D. Truong
	)
Filed: July 27, 2000	)
	)
For: POLYMERIC MATERIALS FOR	)
ELECTROLUMINESCENT DEVICES	)
	)
	)

Mail Stop Appeal Brief--Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

APPEAL BRIEF UNDER 37 C.F.R. § 1.192

In support of the Notice of Appeal filed April 23, 2004, and pursuant to

37 C.F.R. § 1.192, Appellants present in triplicate this brief and enclose herewith a

check for the fee of $320.00 required under 37 C.F.R. § 1.17(c).

This Appeal is filed in response to the final rejection dated October 23, 2003, of

claims 1-7, 9, 11, 12, 14-24, 30, 31 and 33-39, which are set forth in the attached

Appendix. If any additional fees are required or if the enclosed payment is insufficient,

Appellants request that the required fees be charged to Deposit Account No. 06-0916.

I.   Real Party in Interest

Cambridge Display Technology, Ltd. is the assignee of record.

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II.   Related Appeals and Interferences

Appellant's undersigned legal representative knows of no other appeals or

interferences that will directly affect or be directly affected by or have a bearing on the

Board's decision in the pending appeal.

III.   Status of Claims

Claims 1-7, 9, 11-24 and 30-39 are pending in this application.[1] Claim 13 is

objected to as being dependent upon a rejected base claim, but would be allowable if

rewritten in independent form. Claim 32 is allowed. Claims 1-7, 9, 11, 12, 14-24, 30, 31

and 33-39 have been finally rejected under 35 U.S.C. § 103(a).

IV.   Status of Amendments

No amendments have been filed under 37 C.F.R. § 1.116.

V.   Summary of Invention

The present invention is directed to organic polymers for use in electric, optical

and optoelectronic devices, such as polymer-based light-emitting diodes (LED's).

(Specification at p. 1, ll. 2-3.) In particular, the present invention relates to soluble,

adjacently substituted poly(1,4-arylene vinylene)s that have improved optical properties.

(Id. at p. 1, ll. 4-5.) Because of the solubility of the polymers of the present invention,

they have improved processibility for the preparation of devices. (Id. at p. 8, ll. 26-p. 9,

ll. 5.) The improved optical properties of the present invention include efficient

photoluminescence and/or electroluminescence.

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[1] Appellants submitted new claims 33-39 with the response mailed September 10, 2003. The Examiner entered new claims 33-38 without comment. (Office Action mailed October 23, 2003.) Because it appears that the Examiner merely made a typographical error in omitting new claim 39, Appellants treat all of new claims 33-39 as entered and pending in the application.

Organic semiconducting polymers have been used in devices because of their desirable optical properties, such as high photoluminescent quantum yields. In particular, the organic polymer poly(1,4-phenylene vinylene) (PPV) has been used in LED's. (Id. at p. 1, II. 6-16.) A generalized structure of PPV is shown below:
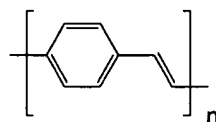
**poly(1,4-phenylene vinylene) (PPV)**

Organic polymers, such as PPVs, are often cast into thin films when incorporated into optical devices. Because many of these polymers are insoluble, they are not solution processible, *i.e.*, they cannot be cast from a solution directly onto a substrate to form thin films of the polymer. Accordingly, thin films of such insoluble polymers were previously prepared via a soluble precursor intermediate; this "two step process" actually adds an extra step and requires exposure to a degrading high temperature environment. First, a monomer is polymerized to form an intermediate soluble precursor polymer. The soluble precursor is dissolved in a solvent, allowing it to be cast into a thin film. The thin film of the soluble precursor polymer is then converted to the final polymer in the form of a thin film of PPV. The conversion can occur by a heat treatment, such as by heating the soluble precursor polymer at 200-300 °C. (Id. at p. 1, I. 23 to p. 2, I. 3; p. 11, Example 3.)

In contrast, soluble PPV polymers have the advantage of being directly solution processible (*e.g.* spin-coated from solution to a thin film of polymer), and do not require any subsequent heat treatment. (E.g., Id. at pg. 9, Example 3.) Thus, formation of the final polymer film only involves one step. However, the known soluble polymers, such

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as poly(2,5-dialkoxy-1,4-phenylene vinylene)s, generally have a photoluminescent

efficiency of only about 15-20% - an undesirably low optical efficiency. (Id. at p. 1, ll.

20-23.)

Accordingly, there remains a need to provide soluble PPV polymers, which are

solution processible, and which have desirable optical properties, e.g., high

photoluminescent and electroluminescent efficiencies.

The inventors have discovered that providing poly(1,4-phenylene vinylene)

polymers with adjacent substituents on the phenylene vinylene unit, e.g. substituents in

the 2 and 3 positions of the phenylene, causes a blue shift in the photoluminescence

and or electroluminescence of the compound and further that solubility can be imparted

to such adjacently substituted PPVs. The 2,3- substitution pattern is illustrated below.
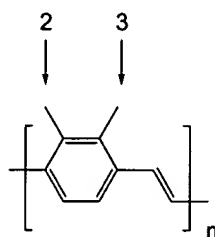
In contrast, many of the prior art PPV polymers contained substituents on the 2,5-

position of the phenylene group. (Id. at p. 3, ll. 3-8.)

Exemplary adjacent substituents, including branched alkyl, aralkyl, and the

corresponding alkoxy derivatives, solubilize the polymer. (Id. at p. 8, ll. 12-13.)

Because the polymers of the present invention are soluble, they allow solution

processing. Moreover, the inventive polymers possess desired optical properties. One

example of the inventive PPV is poly[(2,3-dibutoxy)-1,4-poly(phenylene vinylene)],

which has adjacent butoxy substituents. This PPV is soluble in organic solvents, such

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as chloroform and tetrachloroethane. (Id. at p. 4, ll. 19-22.) Because of its solubility,

the thin film can be cast into a thin film by single-step route without resorting to a soluble

precursor step. (p. 11, Example 3.) Additionally, the soluble, solution processible

polymers of the present invention preclude the need for treatment at high temperatures.

Finally, the polymers of the present invention show useful optical properties, such as

fluorescence emission wavelength and efficiency. (Id. at p. 2, ll. 2-22.)

Accordingly, the polymers of the present invention are soluble film-forming

conjugated poly(1,4-arylene vinylene) compounds having 1,4-phenylene vinylene units

with adjacent substituents. The substituents are oriented so as to affect the electronic

structure sufficiently to cause a blue-shift in the photoluminescence and/or

electroluminescence of the compounds. The present invention also relates to methods

for the production of these compounds, such as polymerizing a bis(halomethyl)

substituted phenyl monomer having adjacent substituents in the presence of a base.

Finally, the present invention relates to components or devices including a compound of

the present invention and/or a method for producing a component or device including

the steps of coating a solution of a compound of the present invention onto a substrate

to form a film.

VI.   Issue

The issue presented for appeal is whether claims 1-7, 9, 11, 12, 14-24, 30, 31

and 33-39 are patentable under 35 U.S.C. § 103(a) over any one of three cited

references: 1) H. Antoniadis, et al. *Poly. Adv. Tech.*, 1997, 8, 392, ("Antoniadis"), 2) W.

C. Wan, et al. *Macromolecules* 1997, 30, 6567 ("Wan"), or 3) B. R. Hsieh, et al. U.S.

Pat. No. 5,558,904 ("Hsieh I").

VII.   Grouping of Claims

Each claim of this application is separately patentable, and upon issuance of a each claim will be entitled to a separate presumption of validity under 35 U.S.C. § 282. For convenience in handling this Appeal, however, the claims will be grouped in 9 groups:

Group I: Claims 1-7, 9, 11, 12, 17-24

Group II: Claims 14-16

Group III: Claim 31

Group IV: Claim 33

Group V: Claim 34

Group VI: Claim 36

Group VII: Claim 37

Group VIII: Claim 38

Group IX: Claim 39

Thus, pursuant to 37 C.F.R. § 1.192(c)(7), in this Appeal, the claims do not all stand or fall together.

VIII.   Argument

The Examiner has rejected claims 1-7, 9, 11, 12, 14-24, 30, 31 and 33-39 as unpatentable under 35 U.S.C. § 103(a) over any one of Antoniadis, Wan or Hsieh I. Each of the independent claims on appeal in the present application recites:

- a soluble,
- film-forming
- conjugated poly(1,4-arylene vinylene) compound having a 1,4-phenylene vinylene unit
- with adjacent substituents,

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- said substituents being oriented such as to affect the electronic structure of the compound sufficiently to cause a blue-shift in the photoluminescence and/or electroluminescence of the compound.

(See, e.g., claim 1.)

Appellants respectfully submit that none of the cited references teach or suggest the claimed combination of a "soluble," adjacently substituted PPV having the claimed electroluminescent and/or photoluminescent characteristics. Furthermore, the Appellants submit that the Examiner has not established any motivation in the references or in the knowledge of those skilled in the art at the time of the invention to make the claimed combination. Accordingly, Appellants request reversal of the rejection of the claims.

A. The § 103 rejection

The Examiner asserts that the claims are obvious in view of each of Antoniadis, Wan and Hsieh I. (Office Action mailed June 10, 2003 at p. 3.)

Wan describes the synthesis of poly[(2,3-diphenyl-p-phenylene)vinylene] (DP-PPV) via an intermediate soluble chlorine precursor, as shown in Scheme I below. (Wan abstract.)

Scheme 1

monomer   soluble precursor polymer   DP-PPV
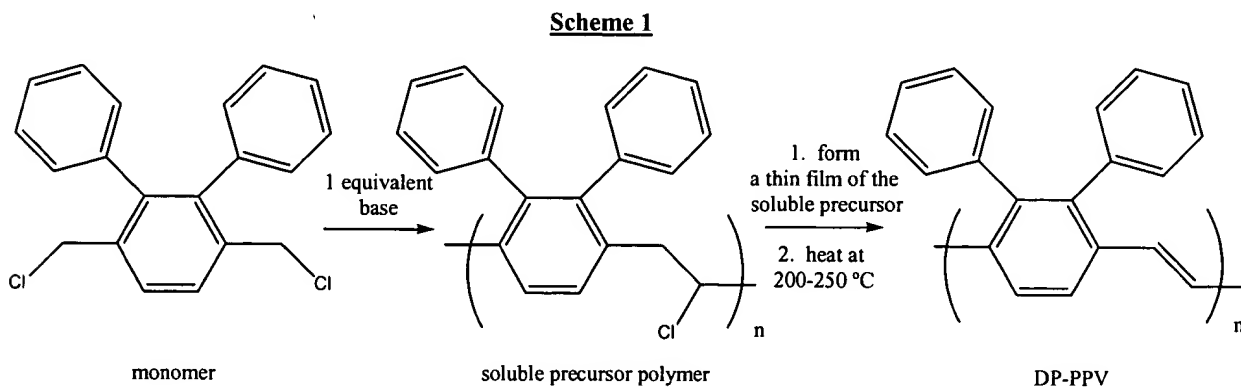
The monomer, 1,4-(bischloromethyl)-2,3-diphenylbenzene, is polymerized in the presence of 1.0 equivalent of a base to yield the soluble chlorine precursor polymer of DP-PPV. (Id.) The soluble precursor polymer is then dissolved in toluene, from which a thin film is cast on a glass substrate. Finally, the thin film of the soluble precursor is heated to 200-250 °C to form a thin film of the final DP-PPV. (Id. at p. 6568.)

Antoniadis describes the preparation of DP-PPV using a two-step soluble chlorine precursor route that is nearly identical to that of Wan. (Antoniadis at p. 392.) The soluble chlorine precursor is prepared by polymerization of the monomer, 1,4-(bischloromethyl)-2,3-diphenylbenzene. (Id. at p. 393.) The soluble chlorine precursor is then converted to DP-PPV by spin-casting into a thin film, followed by heat treatment. (Id.)

Hsieh I also teaches the preparation of DP-PPV using the chlorine precursor route. A solution of the precursor is spin-cast onto a substrate to create a thin film of the precursor. Heat treatment of the precursor at 290 °C yields a thin film of DP-PPV. (Hsieh I, col. 33-34, Example 6.)

Because the polymers of Wan, Antoniadis and Hsieh I, possess adjacent substituents, namely a 2,3-substitution pattern, the Examiner asserts that the cited art discloses compounds having the claimed formulas as well as "the claimed adjacent substituents and the claimed characteristics." (Office Action mailed June 10, 2003 at p. 3.)

B.   None of Antoniadis, Wan or Hsieh I teach or suggest "soluble," adjacently substituted PPV's

All of the present claims include a limitation that the adjacently substituted PPV is "soluble." Appellants respectfully submit evidence that DP-PPV disclosed in Wan,

Hsieh I and Antoniadis is insoluble. Thus, the cited art does not teach the claimed "soluble" compound.

In making a rejection under 35 U.S.C. § 103, the Examiner has the initial burden to establish a *prima facie* case of obviousness. To establish a *prima facie* case of obviousness over a single reference, the Examiner must meet three criteria. First, the Examiner must show some suggestion or motivation, either in the reference itself or in the knowledge generally available to one of ordinary skill in the art, to modify the reference. Second, there must be a reasonable expectation of success. Finally, the prior art reference must teach or suggest all of the claim limitations. (M.P.E.P. § 2143.) This teaching or suggestion to make the claimed combination and the reasonable expectation of success must both be found in the prior art, not in applicant's disclosure. *In re Vaeck*, 947 F.2d 488 (Fed. Cir. 1991).

Appellants respectfully submit that none of the cited references teach or suggest the claimed combination of an adjacently substituted "soluble" PPV. Furthermore, the Examiner has not met his burden of showing a suggestion or motivation in the art to modify any of Antoniadis, Wan or Hsieh I to make the claimed soluble PPV's.

In further support of Appellants' position, Appellants have submitted several pieces of objective evidence to the Examiner demonstrating the *insolubility* of the DP-PPV disclosed in each of Wan, Antoniadis and Hsieh I.

1. Hsieh II

B. Hsieh et al.[2,3] ("Hsieh II") provides direct evidence of the insolubility of the polymers of Wan, Antoniadis and Hsieh I. (Submitted with Response mailed March 3, 2003; attached as Exhibit A.)

Hsieh II describes PPV as "the most popular conjugated polymer" for use in light-emitting diodes. (Hsieh II at p. 231, col. 1.) Hsieh II provides two generalized schemes depicting known methods for preparing PPVs. (Id. at col. 2.) Both schemes involve the initial preparation of a soluble precursor polymer that can be cast into a film, followed by a heat treatment to form the final PPV. (Id. at col. 1.) Hsieh II notes the final PPV is insoluble and that the "precursor approach" has been used for preparing these insoluble PPV films:

> The precursor approach has been used extensively for the fabrication of insoluble PPV films thin films … For example, we have prepared **insoluble** thin films of poly(2,3-diphenyl-p-phenylene vinylene) (DP-PPV) and its derivatives … via a chlorine precursor route.

(Id., emphasis added.) The "insoluble" film referred to by Hsieh II is a PPV where a phenylene group contains adjacent phenyl substituents at the 2,3-position, which has a substitution pattern identical to that of the polymers of Wan, Antoniadis, and Hsieh I. As further confirmation, Hsieh II cites Wan as an example of the prior art insoluble DP-PPV's. (Id.) Thus, Hsieh II unequivocally shows that DP-PPV as described in Wan, Antoniadis and Hsieh I is insoluble, and cannot teach the claimed "soluble" compound, as the Examiner asserted.

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[2] B. Hsieh et al. "A New Family of Highly Emissive Soluble Poly(p-phenylene vinylene derivatives. A Step toward Fully Conjugated Blue-Emitting Poly(p-phenylene vinylenes)." *Journal of the American Chemical Society*, 120:231-232 (1998).

[3] Hsieh II was published after Appellants' priority date of October 21, 1997.

2. Heeger

Heeger et al. ("Heeger")[4] provides additional evidence that the PPV polymers of the cited art are insoluble. (Submitted with Response mailed May 6, 2002; attached as Exhibit B.) Heeger also describes the preparation of PPV based LED's by a "multi-step process". (Heeger at p. 2, l. 13 to p. 3, l. 31.) In this process, a soluble precursor polymer of PPV is cast from solution onto a glass substrate to form a thin film. The substrate with the thin film is then heat treated under vacuum to form the insoluble PPV polymer. Heeger explicitly states that the need to heat treat in excess of 200 °C limits the type of substrate that may be used. For example, heat treatment precludes the use of flexible, transparent polymer substrates. Moreover, heat treatment also may create defects in the final polymer film. These processing disadvantages limit the manufacture of LED's from organic polymers. (Id.)

Heeger attempts to overcome these problems by manufacturing soluble organic polymers, albeit without the use of adjacent substituents. (Id. at p. 4, ll. 29-33.)

Appellants respectfully submit that Heeger evidences the insolubility of PPV polymers in LED's. Those of ordinary skill in the art would understand that Heeger teaches the disadvantages of insoluble polymers, such as the need for a multi-step process and a damaging heat treatment step. Thus, Appellants submit that if DP-PPV were soluble, as asserted by the Examiner, none of Antoniadis, Wan, and Hsieh I would have prepared thin films using the two-step precursor method. Rather, they would have used a single-step process.

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[4] Heeger, "Visible Light Emitting Diodes Fabricated From Soluble Semiconducting Polymers," WO 92/16023, published September 17, 1992.

3.   Wilking

J. Wilking et al (Wilking)[5] explicitly states that PPV's and its derivatives are insoluble due to their highly conjugated structure. (Wilking at ll. 3-5; Submitted with Response mailed May 6, 2002; attached as Exhibit C.) Consequently, these polymers are difficult to process. Wilking specifically describes the preparation of DP-PPV using the two-step soluble precursor route by noting that these insoluble polymers are prepared by heating a soluble precursor polymer. (Id. at ll. 13-17.) Thus, Appellants submit that Wilking provides direct evidence that DP-PPV is insoluble.

4.   Gold

J. F. Gold ("Gold")[6] also describes the problems with insoluble PPV's when making optical devices such as LED's. (Submitted with Response mailed February 24, 2003; attached as Exhibit D.) Gold notes that the step of heat treating the soluble precursor polymer at 200-300 °C can cause defects in the polymer film, which adversely affect the optical properties of devices made from PPV's. (Gold at p. 3.) The two-step precursor method described by Gold is the same method used to prepare DP-PPV in Antoniadis, Wan and Hsieh I. Thus, Gold also evidences the insolubility of DP-PPV.

5.   Declaration of Holmes

Finally, a declaration by Prof. Andrew Holmes states that DP-PPV is insoluble. (Submitted with Response mailed September 10, 2003; attached as Exhibit E.) In his declaration, Prof. Andrew Holmes confirms that DP-PPV as disclosed in Antoniadis,

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[5] Wilking, J. N. et al.,"Comparison of poly(p-phenylene vinylene) and poly(phenylene vinylene) precursors," Conference Proceedings held August 21, 2000, at the 220th ACS National Meeting in Washington, D.C., Submitted with Response mailed May, 06, 2002.
[6] Gold, J. F. "Short Lifetimes of Light Emitting Polymers," www.math.utah.edu/~gold/doc/lep.pdf.

Wan and Hsieh I is an insoluble polymer. Prof. Andrew Holmes further declares that in order for a derivative of PPV to be soluble, it must have solubilizing groups, which enable the polymer to dissolve. The phenyl groups in the 2 and 3 position of DP-PPV do not solubilize the polymer. Appellants submit that the Holmes declaration provides additional evidence that DP-PPV is insoluble.

6. Conclusion

Because the objective evidence set forth above establishes that the polymers of Wan, Antoniadis and Hsieh I are insoluble, there is no teaching or suggestion for soluble PPV polymers, as claimed. Rather, Wan, Antoniadis and Hsieh I teach away from the claimed soluble PPV's. Accordingly, because the cited art does not teach or suggest each and every limitation of the claimed invention, Applicants respectfully submit that a *prima facie* case of obviousness has not been established.

C. The claimed "soluble" limitation is not inherent in the DP-PPV disclosed in Antoniadis, Wan or Hsieh I

The Examiner repeatedly asserts that the prior art DP-PPV disclosed in each of Wan, Antoniadis and Hsieh I inherently disclose the "soluble" limitation of the present invention. (See, e.g., Office Action mailed October 23, 2003, p. 2; Office Action mailed December 24, 2002, p. 3.) Specifically, the Examiner contends, "[s]ince the references do disclose all the requirements for the claimed composition/method, then the claimed 'soluble characteristic' must be considered inherent in the prior art." (Office Action mailed December 24, 2002, p. 3.)

According to the M.P.E.P., to establish inherency, the missing claim limitation must necessarily be present in the prior art. Inherency cannot be established by mere

probabilities or possibilities. (M.P.E.P. 2112.) "In relying upon the theory of inherency, the examiner must provide a basis in fact and/or technical reasoning to reasonably support the determination that the allegedly inherent characteristic <u>necessarily</u> flows from the teachings of the applied prior art." (M.P.E.P. 2112) (quoting *Ex parte Levy*, 17 USPQ2d 1461, 1464 (Bd. Pat. App. & Inter. 1990)).

Once the Examiner rejects a claim based on a reference that teaches a product that appears substantially identical to the claimed product, the Applicant has the burden, and opportunity, to show that the prior art does not possess the alleged inherent feature. The burden of proof on the Applicant is the same whether the rejection is based on inherency under 35 U.S.C. § 102 or on *prima facie* obviousness under 35 U.S.C. § 103. (M.P.E.P. 2112.)

Appellants have provided the Examiner with ample, objective evidence proving that DP-PPV as disclosed in the prior art is insoluble – namely, Hsieh II, Heeger, Wilking, Gold and the Holmes declaration. Thus, Applicants respectfully submit that the "soluble" limitation is not inherent. The Examiner refuses to accept any of this evidence, even though the Examiner has not provided any objective evidence of the solubility of the prior art polymers, or objective evidence discrediting Appellants' evidence.

Instead, the Examiner relies on *In re Best* to support his contention that the DP-PPV of the cited references inherently possesses the claimed "soluble" limitation. (Office Action mailed December 24, 2002.) In *In re Best*, the claims were directed to zeolitic molecular sieve catalysts and a process for preparing them. *In re Best*, 562 F.2d 1252, 1253 (C.C.P.A. 1977). The process claims included the limitation that the

zeolite is heated and then cooled "at a rate sufficiently rapid" that it exhibits a particular X-ray diffraction pattern. *Id.* at 1253. The court found that all of the limitations of the process claim were expressly met by a prior art reference, except for the cooling rate. *Id.* at 1254. The court assumed that the prior art zeolite must be cooled for subsequent handling, and thus the cooling rate was held to be inherent in the reference. *Id.*

The court noted that Best could have overcome the rejection by showing that the prior art process would not produce a zeolite having the claimed X-ray diffraction pattern. *Id.* Best failed to do so. *Id.* Consequently, the court upheld the rejection of the claims as either anticipated under U.S.C. 35 § 102 or obvious under § 103. *Id.*

Contrary to *In re Best*, Appellants in the present case have submitted multiple proofs that the prior art DP-PPV is not soluble - Hsieh II, Heeger, Wilking, Gold and the Holmes declaration are all direct evidence of the insolubility of the prior art polymers. Appellants respectfully submit that this evidence, explained in detail above, proves that the prior art DP-PPV cannot be inherently soluble.

Thus, the objective evidence set forth above establishes that the PPV polymers of Antoniadis, Wan and Hsieh I are insoluble and do not inherently possess the "soluble" limitation. This evidence also distinguishes the present case from the Examiner's reliance on *Best*. The Examiner has not explained why he does not accept any of Hsieh II, Heeger, Wilking, Gold, or the declaration of Holmes as evidence that the "soluble" limitation is not taught or suggested by the prior art.

Accordingly, Applicants respectfully submit that the Examiner has failed to establish a *prima facie* case of obviousness because the cited art does not teach or suggest each and every limitation.

Accordingly, Appellants respectfully request that the rejection under 35 U.S.C.

§ 103 be reversed.

D.   A property of a compound is a patentable limitation

The Examiner has further asserted that the "soluble" limitation "does not mean

anything." (Advisory Action mailed March 21, 2003.) Appellants respectfully disagree

and submit that the claim term "soluble" should be granted patentable weight in the

context of the present claims.

The Federal Circuit has held that a property limitation can distinguish compound

claims from the prior art. *E.I. Du Pont de Nemours & Co., v. Phillips Petroleum Co.*, 849

F.2d 1430, 1435 (Fed. Cir. 1988) In *E.I. Du Pont*, the claims were directed to

copolymers defined in part by their properties. Claim 1 is representative:

> 1. An interpolymer composed of interpolymerized comonomers consisting
> essentially of ethylene and at least one normal aliphatic mono-alpha-olefinic
> hydrocarbon containing from 5 to 10 carbon atoms per molecule, the proportion
> of said monoolefinic hydrocarbon being from 3 to 7% of the weight of the
> interpolymer, **said interpolymer having a melt index within the range of 0.3
> to 20, and, when in the form of a film, an Elmendorf tear strength in the
> range of 150 to 400 grams per mil, and a density of 0.93 to 0.94.**

Id. at 1440 (emphasis added). In *DuPont*, the defendant, relying on *Titanium Metals,*

alleged that its polymers anticipated, and therefore made invalid, claim 1 because the

Elmendorf tear strength limitation was merely a property that could not distinguish over

prior art polymers having the same structural limitations. *Id.* at 1435.

In *Titanium Metals*, the claims were directed to a titanium-based alloy having

specified ranges of nickel, molybdenum and iron, the "alloy being characterized by good

corrosion resistance in hot brine environments." *Titanium Metals Corp. of America v.*

Banner, 778 F.2d 775, at 776. A prior art reference described a titanium alloy within the

claimed percentages of metals, but was silent regarding corrosion resistance. *Id.* The court found the corrosion resistance property inherent in the prior art. *Id.* at 782.

The court in *E.I. Du Pont* clarified *Titanium Metals*, holding that it does not mean that property limitations can never have patentable weight. *Id.* at 1435. The issue in *Titanium* was whether one could patent the discovery of a new property of a known composition of matter. In *E.I. Du Pont*, the issue was "whether the claimed copolymer, as defined in part by various property parameters, is new." *Id.*

The *DuPont* court further held,

> "[o]n occasion, **particularly with polymers**, structure alone may be inadequate to define the invention, making it appropriate to define the invention in part by property limitations." *Id.* (emphasis added). Thus, the Federal Circuit has made clear that compositions, especially polymers, may be defined in terms of both their structure and properties.

Id. at 1436.

Appellants submit that the "soluble" limitation of the present invention is an appropriate property limitation that, along with the claimed structure, more precisely defines the claimed compounds. Thus, contrary to the Examiner's assertion, the term "soluble" should be granted patentable weight.

E.   Additional patentable features

Claims 2-7, 9, 11, 12, 14-24, 30, 31 and 33-39 all recite additional elements, in addition to the "soluble" limitation, that are not taught in the prior art. The Examiner has failed to explain how the prior art makes obvious these additional features. Wan, Antoniadis and Hsieh I do not teach or suggest these additional claim limitations. Thus,

claims 2-7, 9, 11, 12, 14-24, 30, 31 and 33-39 are also patentable based on these additional features.

For example, dependent claim 2 further specifies that the adjacent substituents are independently selected from a group including i) R-, RO-, RS-, and RR'N wherein R and R' are independently a straight or branched chain alkyl group, alkenyl, group, or alkynyl group havein 1-10 carbon atoms, an aryl group or and aromatic or non-aromatic heterocyclic group, and ii) a group in which the adjacent substituents together form a cyclic group, the cyclic group containing 1-10 carbon atoms and 0 to 6 hetero atoms selected from O, S and N. Claim 3, which depends from claim 2, specifies that the cyclic group contains 2-6 hetero atoms. Dependent claim 4 further specifies that one or both of the adjacent substituents is selected from a branched alkyl group and a branched alkoxy group. Dependent claim 5 further specifies that the carbon atoms at the adjacent substituted positions of the aryl until is attached to its substituent via a hetero atom, selected from O, S or N. Dependent claim 6 further specifies that the adjacent substituents are solubilising. Dependent claim 7 further specifies that one or both of the adjacent substituents are independently selected from butyloxy, ethylhexyloxy and 3',7'-dimethyloctyloxy groups. Dependent claim 9 recites that the poly(arylene vinylene) is a co-polymer comprising a fluorescent unit carrying a distyryl-2,3-disubstituted-benzene fragment.

Appellants submit that these additional structural elements of the claimed PPV polymers are nowhere taught or suggested by any of Wan, Antoniadis or Hsieh I.

Dependent claim 11 further specifies that the adjacent substituents are in the 2-position and the 3-position of the phenylene residue. In claim 12, which depends from claim 11, the compound has a structure of formula (I):
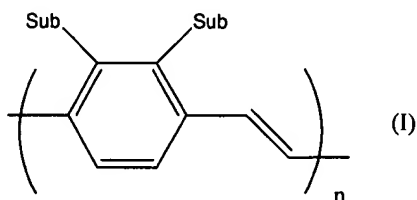
Dependent claim 14 recites a method for producing a compound according to claim I comprising polymerizing a bis(halomethyl) substituted phenyl monomer in the presence of a base, wherein the phenyl monomer has adjacent substituents. Dependent claim 15 specifies that the monomer of method claim 14 is a chloro, bromo, or iodo derivative. Dependent claim 16 recites that the base is potassium teritiary butoxide.

Dependent claim 17 recites a component or device comprising the compound of claim 1. In claim 18, the component or device of claim 17 further comprises an electric, electronic, optical or optoelectronic component or device. Claim 19 specifies that the component or device further comprises a photoluminescent or electroluminescent component or device. In claim 20, a light emitting diode comprises a component or device as defined in claim 17.

Claims 21-24 recite a method for producing a component or device comprising coating a solution of the compound of claim 1 on a substrate to form a film.

Dependent claim 30 recites a light emitting diode having a coating of a compound according to claim 1.

Independent claim 31 recites an electric, electronic, optical or optoelectronic component or device having a coating comprising a soluble, film-forming conjugated

poly(1,4-arylene vinylene) compound having a 1,4-phenylene vinylene unit with adjacent substituents, which produces blue-shifted electroluminescence or photoluminescence.

Independent claim 33 recites a soluble, film-forming conjugated poly(1,4-arylene vinylene) compound having solubilising groups so as to render the conjugated poly(1,4-arylene vinylene) compound soluble and having a 1,4-phenylene vinylene unit with adjacent substituents oriented so as to affect the photoluminescence and/or electroluminescence of the compound.

Independent claim 34 recites a component or device having a coating comprising a soluble, film-forming conjugated poly(1,4-arylene vinylene) compound having solubilising groups so as to render the conjugated poly(1,4-arylene vinylene) compound soluble and having a 1,4-phenylene vinylene unit with adjacent substituents oriented so as to affect the photoluminescence and/or electroluminescence of the compound.

Independent claim 35 recites a compound comprising a film-forming conjugated poly(1,4-arylene vinylene) compound, said poly(1,4-arylene vinylene) being soluble in organic solvents.

Independent claim 36, which is similar to claim 34, further specifies that the poly(1,4-arylene vinylene) compound is soluble in organic solvents.

Independent claim 37 recites a process for directly obtaining a soluble, film-forming conjugated poly(1,4-arylene vinylene) compound having a 1,4-phenylene vinylene unit with adjacent substituents.

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Independent claim 38 recites a soluble, film-forming conjugated poly(1,4-arylene vinylene) compound having solubilising groups so as to render the conjugated polymer soluble in organic solvents.

Finally, independent claim 39 similarly recites a component or device having a coating of a film-forming conjugated poly(1,4-arylene vinylene) compound having solubilising groups so as to render the compound soluble in organic solvents.

F.   Separate patentability of the claim groups

Claims 1-7, 9, 11, 12, 17-24, and 30 are separately patentable. Appellants explicitly argued the patentability of independent claim 1 in response to the Examiner's obviousness rejection, noting that the prior art does not teach or suggest soluble PPV's. (Response mailed November 13, 2002 at p. 3; Response mailed July 11, 2002 at p. 4.)

Appellants argued the patentability of method claim 14 to rebut the Examiner's contention that the reactants and steps of the claimed method are disclosed in the prior art. Appellants noted that the prior art does not disclose a method of making a soluble compound having adjacent substituents. Thus, claims 14-16 are grouped separately. (Response mailed November13, 2002 at p. 3 and 6.)

Appellants specifically argued the patentability of component claim 31 during prosecution. Thus, claim 31 is grouped separately. (Response mailed November 13, 2002 at p. 3; Response mailed July 11, 2002 at p. 4.)

Appellants have grouped each of claims 33-39 individually because their patentability was separately argued upon submission to the Office.

IX. Conclusion

For all of the reasons set forth above, Appellants maintain that the Examiner has failed to establish a *prima facie* case of obviousness over any one of Wan, Antoniadis or Hsieh I. The Examiner has not demonstrated that one of ordinary skill in the art would have been motivated to modify the references to make Appellants' claimed soluble, adjacently substituted PPV's. Nor has the Examiner demonstrated that those of skill in the art would have had any reasonable expectation of success in making the claimed compounds. Further, the Appellant has submitted multiple proofs, none of which the Examiner has discredited, that the prior art compounds are not soluble. Thus, Appellants respectfully request reversal of the rejection of claims 1-7, 9, 11, 12 14-24, 30, 31 and 33-39 under 35 U.S.C. § 103(a).

To the extent any further extension of time under 37 C.F.R. § 1.136 is required to obtain entry of this Appeal Brief, such extension is hereby respectfully requested. If there are any fees due under 37 C.F.R. §§ 1.16 or 1.17 which are not enclosed herewith, including any fees required for an extension of time under 37 C.F.R. § 1.136, please charge such fees to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Date: July 23, 2004

By: _Maria Bault, Reg. No. 52,516_
for Therese A. Hendricks
Reg. No. 30,389

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APPENDIX - PENDING CLAIMS

1.   (previously presented) A compound comprising a soluble, film-forming conjugated poly(1,4-arylene vinylene) compound having a 1,4-phenylene vinylene unit with adjacent substituents, said substituents being oriented such as to affect the electronic structure of the compound sufficiently to cause a blue-shift in the photoluminescence and/or electroluminescence of the compound.

2.   (original) A compound according to claim 1, wherein the substituents are independently selected from:

(i)   R-, RO-, RS-, and RR'N-

wherein R and R' are independently: a straight or branched chain alkyl group, alkenyl group, or alkynyl group having 1-10 carbon atoms; an aryl group; or an aromatic or non-aromatic heterocyclic group; and

(ii)   a group in which the adjacent substituents together form a cyclic group, the cyclic group containing, in addition to the two carbon atoms of the arylene unit to which it is attached, 1-10 carbon atoms and 0 or 1-6 hetero atoms selected from 0, S and N.

3.   (original) A compound according to claim 2, wherein the cyclic group contains 2-6 hetero atoms.

4.   (previously presented) A compound according to claim 1, wherein one or both of the adjacent substituents are independently selected from a branched alkyl group and a branched alkoxy group.

5.   (previously presented) A compound according to claim 1, wherein each of the carbon atoms at the adjacent substituted positions of the aryl unit is attached to its substituent via a hetero atom, selected from O, S or N.

6.   (previously presented) A compound according to claim 1, wherein the substituents are solubilising substituents.

7.   (previously presented) A compound according to claim 1, wherein one or both of the adjacent substituents are independently selected from butyloxy, ethylhexyloxy and 3',7'-dimethyloctyloxy groups.

8.   (canceled).

9.   (previously presented) A compound according to claim 1, wherein the poly(arylene vinylene) is a co-polymer comprising a fluorescent unit carrying a distyryl-2,3-substituted-benzene fragment.

10.   (canceled).

11.   (previously presented) A compound according to claim 1, wherein the adjacent substituents are in the 2-position and the 3-position of the phenylene residue.

12.   (previously presented) A compound according to claim 11, of formula (I):
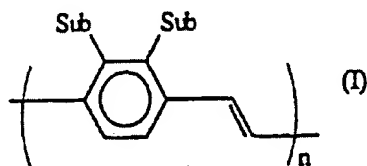
wherein Sub is a substituent as defined in claim 1, the vinylene unit may be a trans vinylene unit or a cis vinylene unit, and n is the number of units of the formula in the polymer.

13.   (original) A compound according to claim 11, of formula (II) or

formula (III):
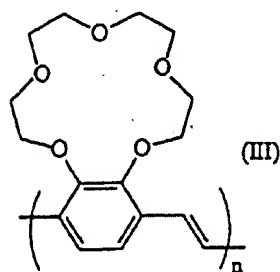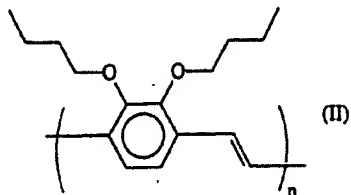
wherein the vinylene unit may be a trans vinylene unit or a cis vinylene unit, and n is the

number of units of the respective formula in the polymer.

14.   (previously presented) A method for the production of a compound

as defined in claim 1, which method comprises polymerising a bis(halomethyl)

substituted phenyl monomer in the presence of a base to form a poly(arylene vinylene),

wherein the phenyl monomer has adjacent substituents on the phenyl residue.

15.   (original) A method according to claim 14, wherein the monomer is

a bis(chloromethyl), bis(bromomethyl) or bis(iodomethyl) monomer.

16.   (previously presented). A method according to claim 14, wherein

the bas is potassium tertiary butoxide.

17.   (previously presented) A component or device comprising a

compound as defined in claim 1.

18.   (previously presented) A component or device according to claim 17, further comprising an electric, electronic, optical or optoelectronic component or device.

19.   (previously presented) A component or device according to claim 17, further comprising a photoluminescent or electroluminescent component or device.

20.   (previously presented) A light emitting diode comprising a component or device as defined in claim 17.

21.   (previously presented) A method for producing a component or device, which method comprises coating a solution of a compound as defined in claim 1 onto a substrate to form a film.

22.   (original) A method according to claim 21, wherein the substrate is ITO.

23.   (previously presented) A method according to claim 21, wherein the solution is a chloroform solution.

24.   (previously presented) A method according to claim 21, wherein the solution is spin-coated onto the substrate.

25-29.   (canceled).

30.   (original) A light emitting diode having a coating of a compound according to claim 1.

31.   (previously presented) An electric, electronic, optical or optoelectronic component or device having a coating comprising a soluble, film-forming conjugated poly(1,4-arylene vinylene) compound having a 1,4-phenylene vinylene unit

with adjacent substituents which produces blue-shifted electroluminescence or photoluminescence.

     32.   (previously presented) A compound comprising a soluble, film-forming conjugated poly(phenylene vinylene) compound having a 1,4-phenylene vinylene unit with adjacent substituents, said substituents being oriented such as to affect the electronic structure of the compound sufficiently to cause a blue-shift in the photoluminescence and/or electroluminesence of the compound, wherein the adjacent substituents are in the 2-position and the 3-position of the phenylene residue, wherein the compound is of formula (II) or formula (III):
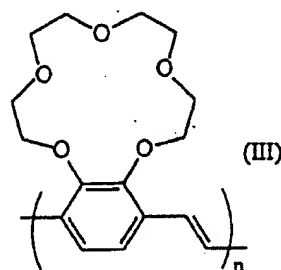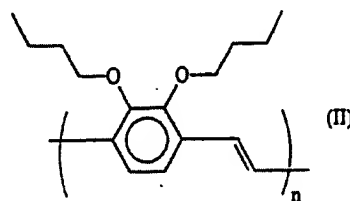
wherein the vinylene unit may be a trans vinylene unit or a cis vinylene unit, and n is the number of units of the respective formula in the polymer.

     33.   (previously presented) A compound comprising a soluble, film-forming conjugated poly(1,4-arylene vinylene) compound having solubilising groups so as to render the conjugated poly(1,4-arylene vinylene) compound soluble and having a 1,4-phenylene vinylene unit with adjacent substituents, said substituents being oriented

such as to affect the electronic structure of the compound sufficiently to cause a blue-shift in the photoluminescence and/or electroluminescence of the compound.

34.   (previously presented) An electric, electronic, optical or optoelectronic component or device having a coating comprising a soluble, film-forming conjugated poly(1,4-arylene vinylene) compound having solubilising groups so as to render the conjugated poly(1,4-arylene vinylene) compound soluble and having a 1,4-phenylene vinylene unit with adjacent substituents which produces blue-shifted electroluminescence or photoluminescence.

35.   (previously presented) A compound comprising a film-forming conjugated poly(1,4-arylene vinylene) compound, said poly(1,4-arylene vinylene) compound being soluble in organic solvents and having a 1,4-phenylene vinylene unit with adjacent substituents, said substituents being oriented such as to affect the electronic structure of the compound sufficiently to cause a blue-shift in the photoluminescence and/or electroluminescence of the compound.

36.   (previously presented) An electric, electronic, optical or optoelectronic component or device having a coating comprising a film-forming conjugated poly(1,4-arylene vinylene) compound, said poly(1,4-arylene vinylene) compound being soluble in organic solvents and having a 1,4-phenylene vinylene unit with adjacent substitutents which produces blue-shifted electroluminescence or photoluminescence.

37.   (previously presented) A process for directly obtaining a soluble, film-forming conjugated poly(1,4-arylene vinylene) compound having a 1,4-phenylene vinylene unit with adjacent substituents, said substituents being oriented such as to affect the electronic structure of the compound sufficiently to cause a blue-shift in the

photoluminescence and/or electroluminescence of the compound, said process comprising a step of dehydrohalogenation condensation polymerisation comprising subjecting a solution comprising 2,3 disubstituted bishalomethylbenzene monomers to polymerisation with at least two equivalents of base.

38.   (previously presented) A compound comprising a soluble, film-forming conjugated poly(1,4-arylene vinylene) compound having solubilising groups so as to render the conjugated poly(1,4-arylene vinylene) compound soluble in organic solvents, the compound having a 1,4-phenylene vinylene unit with adjacent substituents, said substituents being oriented such as to affect the electronic structure of the compound sufficiently to cause a blue-sift in the photoluminescence and/or electroluminescence of the compound.

39.   (previously presented) An electric, electronic, optical or optoelectronic component or device having a coating comprising a film-forming conjugated poly(1,4-arylene vinylene) compound having solubilising groups so as to render the conjugated poly(1,4-arylene vinylene) compound soluble in organic solvents and having a 1,4-phenylene vinylene unit with adjacent substituents which produces blue-shifted electroluminescence or photoluminescence.

J. Am. Chem. Soc. 1998, *120*, 231–232

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A New Family of Highly Emissive Soluble
Poly(p-phenylene vinylene) Derivatives. A Step
toward Fully Conjugated Blue-Emitting
Poly(p-phenylene vinylenes)

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Gregory M. Schaaf,[§] and William A. Feld[§]

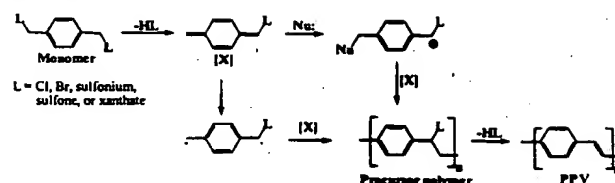Xerox Corporation, 800 Phillips Road, 114-39D
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Poly(p-phenylene vinylene) (PPV) is the first conjugated polymer reported for the application in light-emitting diodes.[1] Today, PPV and its derivatives remain as the most popular conjugated polymer class for this application. This is due heavily to the development of several ingeniously elegant synthetic routes toward the fabrications of PPV thin films.[2] Many of these routes involve 1,6-polymerization of p-xylylenes to form poly(p-phenylene vinylenes) (PPVs).[3] A general scheme for such polymerization processes is shown in Scheme 1. The polymerization of a bis-sulfonium or a bis-halomethyl monomer in the presence of a base was reported independently in the mid-1960s.[2–4] The polymerization of sulfone or xanthate-type monomers was reported recently.[5–7] A bis-halomethyl type monomer can also be polymerized via vapor phase deposition polymerization to give a PPV.[2,3] In the case of the solution polymerization, a monomer undergoes 1,6-elimination of HL in the presence of a large excess base to form the corresponding p-xylylene [X], which undergoes radical and/or anionic 1,6-polymerization along with 1,2-elimination of HL to give a PPV. This one-step approach has been used for the synthesis of soluble PPVs with flexible side groups.[8] One can also carry out the 1,6-polymerization and the 1,2-elimination separately to obtain a soluble precursor polymer first and then cast it into thin film and convert it to the corresponding PPV. This precursor approach has been used extensively for the fabrication of insoluble PPV thin films.[2] For example, we have prepared insoluble thin films of poly(2,3-diphenyl-p-phenylene vinylene) (DP-PPV) and its derivatives (Scheme 2) via a chlorine precursor route (CPR).[9]

Here, we report the synthesis of the first series of a new family of soluble DP-PPV derivatives, namely poly(2,3-diphenyl-5-hexyl-
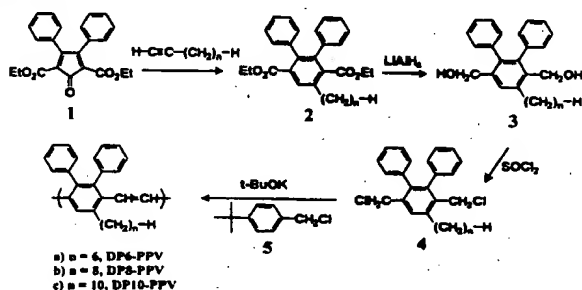
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§ Wright State University.
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Scheme 1

Scheme 2

Scheme 3

p-phenylene vinylene) (DP6-PPV) and its derivatives via a versatile synthetic methodology that involves two key steps: first, the synthesis of new alkylated DP-PPV monomers via the Diels–Alder reaction; second, the polymerization of the monomers via a modified Gilch route involving the use of an acidic additive, such as 4-tert-butylbenzyl chloride.[10] Amazingly, DP6-PPV shows very high photoluminescence (PL) quantum efficiency of 65% in the solid state.

As shown in Scheme 3, the Diels–Alder reaction of 2,5-bis-(ethoxycarbonyl)-3,4-diphenylcyclopentadienone (1) with 1-octyne, 1-decyne, or 1-dodecyne gives 2a–c in 95–97% yields. They are reduced with LiAlH₄ to give 3a–c and then reacted with SOCl₂ in methylene chloride to give monomer 4a–c in 22–50% overall yields. This may be the first report on the use of the Diels–Alder reaction to introduce flexible solubilizing side groups onto monomers. Typically, flexible side groups have been introduced by alkylation of hydroxy groups [8a,11] or Ni-catalyzed coupling of an aromatic bromide with an alkyl Grignard reagent.[12] Our synthetic sequence is very versatile and offers the possibility of introducing virtually any functional group or chromophore into 1,4-bis(chloromethyl)benzene monomers routinely.[9] With a simple access to a wide range of monomers, DP-PPV derivatives are becoming the most fertile family of PPV derivatives.

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Table 1. Polymerization Parameters and the Molecular Weights of DPn-PPVs

	mono-mer	5/4//THF (mg/g//mL)	molar ratio 5:4	1.0 M t-BuOK in THF (mL)[a]	M_w/M_n (×10³)[b]	PD	yield
1	4a−c	0.0/0.3//15		4.4	gel		
2	4a	7.5/0.3//15	0.056	4.4	>2000		71
3	4a	67/0.3//15	0.51	4.4	1060/330	3.20	66
4	4a	89/0.3//15	0.67	4.4	988/300	3.29	50
5	4a	133/0.3/15	1.00	4.4	350/110	3.18	45
6	4b	136/0.33//15	1.00	4.4	571/150	3.80	40
7	4c	182/0.47/16	1.00	4.4	404/123	3.28	71

[a] The base was added all at once into an ice—water-cooled and magnetically stirred solution of 5/4//THF. [b] Relative to polystyrene in CH₃Cl.

Scheme 4
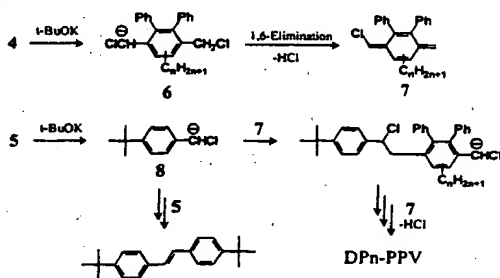
. As shown in Table 1, entry 1, a typical Gilch route that involves the polymerization of 4a−c with a large excess of t-BuOK gives insoluble DPn-PPV gels. We overcame this problem by using a modified Gilch route involving the use of a nonpolymerizable acidic additive in the polymerization.[10] Entries 2−5 using $tert$-butylbenzyl chloride (5) as the acidic additive, show that soluble high molecular weight DP6-PPVs with relatively narrow molecular weight distribution are obtained. Similarly, soluble DP8-PPV (entry 6) and DP10-PPV (entry 7) were prepared. The molecular weight of DP6-PPV decreases as the molar ratio of 5:4a increases. This can be accounted for by the anionic polymerization mechanism shown in Scheme 4. Deprotonation of a chloromethyl proton in 4 gives an anionic intermediate 6, which undergoes a 1,6-dehydrochlorination to give p-xylylene 7. Deprotonation of 5 produces 8, which can nucleophilically attack 7 to initiate anionic polymerization to give DPn-PPV with $tert$-butyl chain ends or attack 5 followed by 1,2-dehydrochlorination to give 4,4′-di-$tert$-butylstilbene as a side product.[4b] The formation of the stilbene is one possible reason for the formation of high polymers even in the presence of a large amount of 5. The other possibility is the involvement of radical polymerization of 7 as reported for the analogous sulfonium precursor routes and sulfone precursor routes.[13,14]

Although the soluble DP-PPV derivatives shown in Table 1, entries 2−7, were isolated by a single precipitation of the reaction mixtures into methanol, they still showed very high purity according to elemental analysis. For example, DP6-PPV shows that elemental analysis data of C 90.47, H 7.53, Cl 0.14 are in agreement with C 92.26, H 7.74 as calculated for [C₂₆H₂₆]n. This result indicates that the soluble DP6-PPVs obtained from the modified Gilch route have very high purity and very low chlorine content, which implies a high degree of conversion of greater than 99.0%.
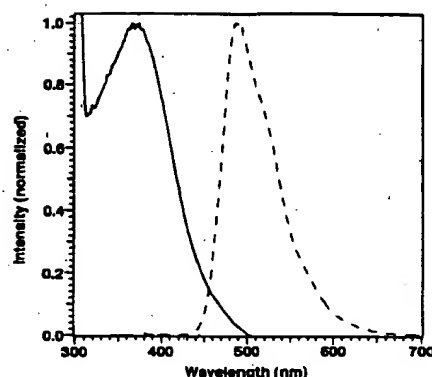
Figure 1. UV—vis (solid line) and photoluminescence (PL) (dotted line) spectra of a DP6—PPV thin film (intensities are normalized).

The UV—vis and PL spectra of a DP6-PPV thin film are shown in Figure 1. The bluish-green emission peak at 490 nm for DP6-PPV is about 10 nm blue shifted with respect to that of DP-PPV.[9b] This is attributable to the steric effect of the n-hexyl group that reduces the effective conjugation length. To our best knowledge, the 490 nm emission for DP6-PPV is the bluest PL emission for a fully conjugated PPV. Through the introduction of more steric hindrance, a blue emitting (<480 nm), fully conjugated PPV may be possible. This intriguing possibility is being explored in our laboratory. Blue-emitting materials are particularly useful for designing multicolor electroluminescent devices.[15]

Excited at 370 nm, DP6-PPV thin films showed a very high PL quantum efficiency of 65%. This is one of the highest PL efficiencies reported for PPVs. For comparison, the solid-state PL efficiencies for PPV, poly(2-methoxy-5-((2′-ethylhexyl)oxy)-p-phenylene vinylene) (MEH-PPV), poly((2-dimethyloctyl)silyl-p-phenylene vinylene) are 15, 27, and 60%, respectively.[16] The high PL quantum efficiency for DP6-PPV may be due to the steric effect of the two phenyl rings and the alkyl groups, which can prevent self-quenching processes, induced by closely packed emissive segments.[17] It has been reported that closely packed conjugated polymers are prone to the formation of exciplexes or polaron pairs that can serve as quenching sites.[17]

In summary, we have reported the synthesis of DP6-PPV, DP8-PPV, and DP10-PPV as the first series of a new family of soluble, highly emissive DP-PPV derivatives. The key synthetic steps are the monomer synthesis via the Diels—Alder reaction and the polymerization via a modified Gilch route involving an anionic polymerization mechanism. The polymers were obtained in 40—70% yields and showed very high molecular weights and purity. The PL emission peak of 490 nm may represent the bluest emission peak reported for a fully conjugated PPV. The PL efficiency of 65% for DP6-PPV is among the highest values reported for a fully conjugated PPV.

Supporting Information Available: Experimental details (5 pages). See any current masthead page for ordering and Internet access instructions.

JA973553R

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H01L 33/00, 29/28, H01J 1/62 H01J 63/04	**A1**	(43) International Publication Date:	17 September 1992 (17.09.92)

(54) Title: VISIBLE LIGHT EMITTING DIODES FABRICATED FROM SOLUBLE SEMICONDUCTING POLYMERS

(57) Abstract

Visible light LEDs are produced having a layer of conjugated polymer which is cast directly from solution or formed as a gel-processed admixture with a carrier polymer. The LEDs can be formed so as to emit polarized light.

5   VISIBLE LIGHT EMITTING DIODES FABRICATED FROM
                   SOLUBLE SEMICONDUCTING POLYMERS

         Field of the Invention
                 This invention relates generally to light-
10   emitting diodes and their fabrication. More
      particularly, it concerns light-emitting diodes
      fabricated from semiconducting (conjugated) polymers
      which are soluble in common organic solvents, and yet
      more particularly to the fabrication of such diodes on
15   flexible polymer substrates.

         Background of the Invention
                 Solid-state light-emitting diodes (LEDs) have
      found widespread application in displays, as well as in a
20   variety of less common applications. Currently, LEDs
      are fabricated from conventional semiconductors; for
      example, gallium arsenide (GaAs), typically doped with
      aluminum, indium, or phosphorus. Using this technology,
      it is very difficult to make large area displays. In
25   addition, the LEDs made of these materials are typically
      limited to the emission of light at the long wavelength
      end of the visible spectrum. For these reasons, there
      has been considerable interest for many years in the
      development of suitable organic materials for use as the
30   active (light-emitting) components of LEDs. (See
      references 1-6). The need for relatively high voltages
      (i.e., voltages incompatible with digital electronics)
      for the onset of light emission has been a hindrance to
      the commercialization of LEDs fabricated from organic
35   materials.

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The utilization of semiconducting organic polymers (i.e., conjugated polymers) in the fabrication of LEDs expands the use of organic materials in electroluminescent devices and expands the possible

5   applications for conducting polymers into the area of active light sources, (see Reference 7) with the possibility of significant advantages over existing LED technology. Controlling the energy gap of the polymer, either through the judicious choice of the conjugated

10 backbone structure or through side-chain functionalization, should make possible the emission of a variety of colors throughout the visible spectrum.

In the prior art, Tomozawa et al (see Reference 8) disclosed diodes fabricated by casting semiconducting

15 polymers from solution.

Also in the art, Burroughs et al (see Reference 7) disclosed a multi-step process in the fabrication of LED structures characterized as follows:

      1)   A glass substrate is utilized. The

20   substrate is pre-coated with a transparent conducting layer of indium/tin oxide (ITO). This ITO coating, having high work function serves as the ohmic hole-injecting electrode.

25   2)   A soluble precursor polymer to the conjugated polymer, poly(phenylene vinylene), PPV, is cast from solution onto the substrate as a thin, semitransparent layer (approximately 100-200 nm).

30   3)   The precursor polymer is converted to the final conjugated PPV by heat treating the precursor polymer (already formed as a thin film on the substrate) to temperatures in excess of $200^\circ C$ while

35   pumping in vacuum.

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Summary of the Invention

        It is accordingly an object of the present
invention to overcome the aforementioned disadvantages of
the prior art and, primarily, to provide light-emitting
diodes fabricated from semiconducting polymers which are
soluble in the conjugated form and therefore require no
subsequent heat treatment at elevated temperatures.

        It is additionally an object of the present
invention to utilize the processing advantages associated

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with the fabrication of diode structures from soluble
semiconductor polymers cast from solution to enable the
fabrication of large active areas.

It is additionally an object of the present
5   invention to provide light-emitting diodes fabricated
from semiconducting polymers using flexible organic
polymer substrates.

It is additionally an object of the present
invention to provide methods for the fabrication of
10   light-emitting diodes fabricated from semiconducting
polymers which turn on at bias voltages compatible with
digital electronics (i.e., at voltages less than 5
volts).

Additional objects, advantages and novel
15   features of the invention will be set forth in part in
the description which follows, and in part will become
apparent to those skilled in the art on examination of
the following, or may be learned by practice of the
invention. The objects and advantages of the invention
20   may be realized and attained by means of the
instrumentalities and combinations particularly pointed
out in the appended claims.

In one aspect this invention provides a process
for fabricating light-emitting diodes (LEDs). In this
25   embodiment the process involves a process for fabrication
of light-emitting diodes which emit visible light. This
process comprises the steps of:

i)   precoating a substrate with a transparent
conducting first layer having high work function and
30   serving as an ohmic hole-injecting electrode;

ii)   casting upon the first layer directly from
solution, a thin transparent layer of a soluble
conjugated polymer; and

iii)   fabricating a negative, electron-
35   injecting contact onto the conjugated polymer film. This

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film. This contact is fabricated from a low work function
metal and acts as the rectifying contact in the diode
structure.

In another general aspect this invention
provides the LEDs fabricated by any of these processes.
In a more particular aspect of this invention, the LED
devices employ
poly(2-methoxy,5-(2'-ethyl-hexyloxy)-1,4-phenylene
vinylene), MEH-PPV, as the conjugated polymer. MEH-PPV
offers the advantage of being a conjugated polymer which
is soluble in organic solvents. LED device fabrication
is simplified because of the direct casting of the
conjugated polymer from solution.

Surprisingly, it was found that by using
calcium as the low work function rectifying contact, and
by using ITO coated PET films as the substrate, flexible
LED structures are fabricated which benefit from the
excellent mechanical properties of both the polymer
substrate and the conjugated polymer semiconducting layer
and which exhibit the advantageous characteristics of a
turn-on voltage reduced to 3-4 volts (i.e TTL
compatible), and a quantum efficiency which is improved
by more than an order of magnitude to values of
approximately 1%.

Specific advantages of this invention over the
prior art include the following:

(i)   Because the luminescent semiconducting
       polymer is soluble in its final conjugated
       form, there is no need for heat treatment
       at elevated temperatures. This greatly
       simplifies the fabrication procedure and
       enables a continuous manufacturing
       process.

(ii)   Since the luminescent semiconducting
       polymer layer can be cast onto the

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substrate directly from solution at room
temperature, the LED structure can be
fabricated on a flexible transparent
polymer substrate. These polymer films
5   are manufactured as large area continuous
films. Thus, the use of flexible polymer
films as substrate enables the fabrication
of large area polymer LEDs using either a
batch process or a continuous process.
10   (iii) The use of Calcium as the low work
function contact onto MEH-PPV as the
luminescent polymer leads to unexpected
improvements in the efficiency of the device
and in the compatibility of the device with
15   modern digital electronic circuitry.

Detailed Description of the Invention

The Substrates
20   In some embodiments, the conjugated polymer-
based LEDs are prepared on a substrate. The substrate
should be transparent and nonconducting. It can be a
rigid material such as a rigid plastic including rigid
acrylates, carbonates, and the like, rigid inorganic
25   oxides such as glass, quartz, sapphire, and the like. It
can also be a flexible transparent organic polymer such
as polyester - for example polyethyleneterephthalate,
flexible polycarbonate, poly (methyl methacrylate),
poly(styrene) and the like.
30   The thickness of this substrate is not
critical.

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The Conjugated Polymer

The invention provides LEDs based on conjugated polymers.

In one embodiment the conjugated polymer is cast directly from a solution onto a precooled substrate to form a substrate-supported film.

In another, the conjugated polymer is present as a free-standing film.

In a third embodiment, the conjugated polymer is present as a component of a gel-processed admixture with a carrier polymer and the film is formed from this admixture. This embodiment offers an easy way to obtain aligned conjugated polymer structures which lead to LEDs which can emit polarized light.

The conjugated polymers used herein include soluble conjugated polymers known in the art. These include, for example, poly(2-methoxy,5-(2'-ethyl-hexyloxy)-p-phenylenevinylene) or "MEH-PPV", P3ATs, poly(3-alkylthiophenes) (where alkyl is from 6 to 16 carbons), such as poly(2,5-dimethoxy-p-phenylene vinylene)-"PDMPV", and poly(2,5-thienylenevinylene); poly(phenylenevinylene) or "PPV" and alkoxy derivatives thereof; and polyanilines.

Of these, the MEH-PPV materials are preferred. The preparation of MEH-PPV is given in the examples herein.

The conjugated polymer can be deposited or cast directly from solution. The solvent employed is one which will dissolve the polymer and not interfere with its subsequent deposition.

Typically, organic solvents are used. These can include halohydrocarbons such as methylene chloride, chloroform, and carbon tetrachloride, aromatic hydrocarbons such as xylene, benzene, toluene, other hydrocarbons such as decaline, and the like. Mixed solvents can be used, as well. Polar solvents such as

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water, acetone, acids and the like may be suitable.
These are merely a representative exemplification and the
solvent can be selected broadly from materials meeting
the criteria set forth above.

When depositing the conjugated polymer on a
substrate, the solution can be relatively dilute, such as
from 0.1 to 20% w in concentration, especially 0.2 to
5% w. Film thicknesses of 50-400 and 100-200 nm are
used.

The Carrier Polymer.

In some embodiments, the conjugated polymer is
present in admixture with a carrier polymer.

The criteria for the selection of the carrier
polymer are as follows. The material should allow for
the formation of mechanically coherent films, at low
concentrations, and remain stable in solvents that are
capable of dispersing, or dissolving the conjugated
polymers for forming the final film. Low concentrations
of carrier polymer are preferred in order to minimize
processing difficulties, i.e., excessively high viscosity
or the formation of gross inhomogeneities; however the
concentration of the carrier should be high enough to
allow for formation of coherent structures. Preferred
carrier polymers are high molecular weight (M.W.
>100,000) flexible chain polymers, such as polyethylene,
isotactic polypropylene, polyethylene oxide, polystyrene,
and the like. Under appropriate conditions, which can be
readily determined by those skilled in the art, these
macromolecular materials enable the formation of coherent
structures from a wide variety of liquids, including
water, acids, and numerous polar and nonpolar organic
solvents. Films or sheets manufactured using these
carrier polymers have sufficient mechanical strength at
polymer concentrations as low as 1%, even as low as 0.1%,

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by volume to enable the coating and subsequent processing
as desired.

Mechanically coherent films can also be
prepared from lower molecular weight flexible chain
5   polymers, but generally, higher concentrations of these
carrier polymers are required.

Selection of the carrier polymer is made
primarily on the basis of compatibility of the conjugated
polymer, as well as with the solvent or solvents used.
10   For example, blending of polar conducting polymers
generally requires carrier structures that are capable of
co-dissolving with or absorbing polar reactants.
Examples of such coherent structures are those comprised
of poly(vinyl alcohol), poly(ethylene oxide),
15   poly-para(phenylene terephthalate), poly-para-benzamide,
etc., and suitable liquids. On the other hand, if the
blending of the final polymer cannot proceed in a polar
environment, nonpolar carrier structures are selected,
such as those containing polyethylene, polypropylene,
20   poly(butadiene), and the like.

Turning now to the issue of concentration, it
is of crucial importance that the carrier structure
formed have sufficient mechanical coherence for further
handling during the formation of the final polymer blend.
25   Therefore, the initial concentration of the carrier
polymer generally is selected above 0.1% by volume, and
more preferably above about 0.75% by volume. On the
other hand, it is not desirable to select carrier polymer
concentrations exceeding 90% by volume, because this has
30   a diluting effect on the final conjugated polymer
composite product. More preferably, the concentration of
the carrier polymer in the solution is below 50% by
volume, and still more preferably below 25% by volume.

Thus, solution is provided by dissolving a
35   selected carrier polymer and conjugated polymer in a

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compatible solvent (or mixed solvents) to a predetermined
concentration (using the aforementioned guidelines). In
the present process the "compatible solvent" is a solvent
system into which a desired quantity of soluble

5   conjugated polymer (or soluble precursor polymer) can be
dissolved. The solvent system is also one in which the
carrier polymer is substantially soluble, and will not
interfere with the subsequent structure formation
process. The carrier solution is formed into selected

10   shape, e.g. a fiber, film or the like, by extrusion or by
any other suitable method. The solvent is then removed
(through evaporation, extraction, or any other convenient
method).

          Gels can be formed from the carrier conjugate

15   solution in various ways, e.g., through chemical
crosslinking of the macromolecules in solution, swelling
of cross-linked macromolecules, thermoreversible
gelation, and coagulation of polymer solutions. In the
present invention, the two latter types of gel formation

20   are preferred, although under certain experimental
conditions, chemically crosslinked gels may be preferred.
          Thermoreversible gelation refers to the
physical transformation of polymer solution to polymer
gel upon lower of the temperature of a homogeneous

25   polymer solution (although in exceptional cases a
temperature elevation may be required). This mode of
polymer gelation requires the preparation of a
homogeneous solution of the selected carrier polymer in
an appropriate solvent according to standard techniques

30   known to those skilled in the art. The polymer solution
is cast or extruded into a fiber, rod or film form, and
the temperature is lowered to below the gelation
temperature of the polymer in order to form coherent
gels. This procedure is well known and is commercially

35   employed, e.g., for the formation of gels of high

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molecular weight polyethylene in decalin, paraffin oil,
oligomeric polyolefins, xylene, etc., as precursors for
high strength polyolefin fibers and films.

"Coagulation" of a polymer solution involves
5   contacting the solution with a nonsolvent for the
dissolved polymer, thus causing the polymer to
precipitate. This process is well known, and is
commercially employed, for example, in the formation of
rayon fibers and films, and spinning of high-performance
10   aramid fibers, etc.

Frequently, it is desirable to subject the
carrier polymer/conducting polymer composite to
mechanical deformation, typically by stretching, during
or after the initial forming step. Deformation of
15   polymeric materials is carried out in order to orient the
macromolecules in the direction of draw, which results in
improved mechanical properties. Maximum deformations of
thermoreversible gels are substantially greater than melt
processed materials.(P. Smith and P.J. Lemstra, Colloid
20   and Polym. Sci., 258, 891, (1980).) The large draw
ratios possible with thermoreversible gels are also
advantageous if composite materials may be prepared with
materials limited in their drawability due to low
molecular weights. In the case of conducting polymers,
25   not only do the mechanical properties improve, but, more
importantly, the electrical conductivity also often
displays drastic enhancement by tensile drawing and the
orientation of the conjugated polymer gives rise to LEDs
which will emit polarized light because of the
30   orientation.

The Transparent Conducting First Layer.

The conjugated polymer layer of the LEDs of
this invention is bounded on one surface by a transparent
35   conducting first layer.

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When a substrate is present, this layer is
between the substrate and the conjugated polymer layer.
This first layer is a transparent conductive layer made
of a high work function material that is a material with
5   a work function above 4.5 eV. This layer can be a film
of an electronegative metal such as gold or silver, with
gold being the preferred member of that group. It can
also be formed of a conductive metal-metal oxide mixture
such as indium-tin oxide.
10 These layers are commonly deposited by vacuum
sputtering (RF or Magnetron) electron beam evaporation,
thermal vapor deposition, chemical deposition and the
like.
The ohmic contact layer should be low
15 resistance: preferably less than 300 ohms/square and more
preferably less than 100 ohms/square.

The Electron Injecting Contact
On the other side of the conjugated polymer
20 film an electron-injecting contact is present. This is
fabricated from a low work function metal or alloy (a low
work function material has a work function below 4.3.
Typical materials include indium, calcium, barium and
magnesium, with calcium being a particularly good
25 material. These electrodes are applied by using methods
well-known to the art (e.g. evaporated, sputtered, or
electron-beam evaporation) and acting as the rectifying
contact in the diode structure.

30   Examples
This invention will be further described by the
following examples. These are intended to embody the
invention but not to limit its scope.

35

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Example 1

This example involves the preparation of
poly(2-methoxy,5-(2'-ethylhexyloxy)-p-phenylenevinylene)
"MEH-PPV".

Monomer Synthesis

1. ### Preparation of 1-Methoxy-4-(2-Ethyl-Hexyloxy)Benzene

A solution of 24.8 g (0.2 mole) of 4-methoxy
phenol in 150 ml dry methanol was mixed under nitrogen
with 2.5 M solution of sodium methoxide (1.1 equivalent)
and refluxed for 20 min. After cooling the reaction
mixture to room temperature, a solution of 2-
ethylbromohexane (42.5 ml, 1.1 equivalent) in 150 ml
methanol was added dropwise. After refluxing for 16 h,
the brownish solution turned light yellow. The methanol
was evaporated and the remaining mixture of the white
solid and yellow oil was combined with 200 ml of ether,
washed several times with 10% aqueous sodium hydroxide,
H_2O and dried over $MgSO_4$. After the solvent was
evaporated, 40 g (85%) of yellow oil was obtained. The
crude material was distilled under vacuum (2.2 mm Hg,
b.p. 148-149°C), to give a clear, viscous liquid. ^{1}H NMR
($CDCl_3$) δ 6.98 (4H, s, aromatics), 3.8 (5H, t, $O-CH_2$, O-
CH_3), 0.7-1.7 (15 H, m, C_7H_{15}. IR (NaCl plate) 750, 790,
825, 925, 1045, 1105, 1180, 1235, 1290, 1385, 1445, 1470,
1510, 1595, 1615, 1850, 2030, 2870, 2920, 2960, 3040.
MS. Anal. Calc. for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23; O,
13.54. Found: C, 76.38; H, 10.21; O, 13.45.

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2. <u>Preparation of 2,5-bis(Chloromethyl)-1-Methoxy-4-</u>
   <u>(2-Ethyl-Hexyloxy)Benzene</u>

       To the solution of 4.9 g (20.7 mmoles) of
compound (1) in 100 ml p-dioxane cooled down to 0-5°C, 18
5 ml of conc. HCl, and 10 ml of 37% aqueous formalin
solution was added. Anhydrous HCl was bubbled for 30
min, the reaction mixture warmed up to R.T. and stirred
for 1.5-2 h. Another 10 ml of formalin solution was
added and HCl gas bubbled for 5-10 min at 0-5°C. After
10 stirring at R.T. for 16 h, and then refluxed for 3-4 h.
After cooling and removing the solvents, an off-white
"greasy" solid was obtained. The material was dissolved
in a minimum amount of hexane and precipitated by adding
methanol until the solution became cloudy. After
15 cooling, filtering and washing with cold methanol, 3.4 g
(52%) of white crystalline material (mp 52-54°C) was
obtained. ^{1}H NMR (CDCl$_3$) δ 6.98 (2H, s, aromatics), 4.65
(4H, s, CH$_2$-Cl), 3.86 (5H, t, O-CH$_3$, O-CH$_2$), 0.9-1.5
(15H, m, C$_7$H$_{15}$), IR (KBr) 610, 700, 740, 875, 915, 1045,
20 1140, 1185, 1230, 1265, 1320, 1420, 1470, 1520, 1620,
1730, 2880, 2930, 2960, 3050. MS. Anal. Calc. for
C$_{17}$H$_{26}$O$_2$Cl$_2$:   C, 61.26; H, 7.86; O, 9.60; Cl, 21.27.
Found: C, 61.31; h, 7.74; O, 9.72; Cl, 21.39.

25 <u>Polymerization</u>
   <u>Preparation of Poly(1-Methoxy-4-(2-Ethylhexyloxy-2,5-</u>
   <u>Phenylenevinylene) MEH-MPV</u>

       To a solution of 1.0 g (3 mmol) of 2,5-
bis(chloromethyl)-methoxy-4-(2-ethylhexyloxy)benzene in
30 20 ml of anhydrous THF was added dropwise a solution of
2.12 g (18 mmol) of 95% potassium <u>tert</u>-butoxide in 80 ml
of anhydrous THF at R.T. with stirring. The reaction
mixture was stirred at ambient temperature for 24 h and
poured into 500 ml of methanol with stirring. The
35 resulting red precipitate was washed with distilled water

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and reprecipitated from THF/methanol and dried under
vacuum to afford 0.35 g (45% yield). UV (CHCl$_3$) 500. IR
(film) 695, 850, 960, 1035, 1200, 1250, 1350, 1410, 1460,
1500, 2840, 2900, 2940, 3040. Anal. Calc. for C$_{17}$H$_{24}$O$_2$:

5   C, 78.46; H, 9.23. Found: C, 78.34; H, 9.26.
          Molecular weight (GPC vs. polystyrene) 3 x 10^5.
Inherent viscosity ~ 5 dl/g (but time dependent due to
the tendency to form aggregates). As is the case with a
few other stiff chain polymers, the viscosity increases

10   with standing, particularly in benzene. The resulting
solution is therefore thixotropic.
          The conjugated polymer is highly colored
(bright red-orange).

15   Example 2
     Preparation of MEH-PPV via a precursor polymer route.

Monomer Synthesis
          The monomer synthesis is exactly the same as in
20   Example 1.

Polymerization of the Precursor Polymer and Conversion to
MEH-PPV
          A solution of 200 mg (0.39 mmol) of the monomer
25   salt of Example 1 in 1.2 ml dry methanol was cooled to
0°C for 10 min and a cold degassed solution of 28 mg (1.7
equivalents) of sodium hydroxide in 0.7 ml methanol was
added slowly. After 10 min the reaction mixture became
yellow and viscous. The above mixture was maintained at
30   0°C for another 2-3 h and then the solution was
neutralized. A very thick, gum-like material was
transferred into a Spectrapore membrane (MW cutoff
12,000-14,000) and dialyzed in degassed methanol
containing 1% water for 3 days. After drying in vacuo,
35   70 mg (47%) of "plastic" yellow precursor polymer

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material was obtained. UV (CHCl$_3$) 365. IR (film) 740,
805, 870, 1045, 1075, 1100, 1125, 1210, 1270, 1420, 1470,
1510, 2930, 2970, 3020. Soluble in C$_6$H$_5$Cl, C$_6$H$_3$Cl$_3$,
CH$_2$Cl$_2$, CHCl$_3$, Et$_2$O, THF. Insoluble in MeOH.

5   The precursor polymer was converted to the
conjugated MEH-PPV by heating to reflux (approx. 214°C)
in 1,2,4-trichlorobenzene solvent. The product was
identical with the material obtained in Example 1.

10   Example 3
           Light-emitting diodes (LEDs) were fabricated
consisting of a rectifying indium (work function = 4.2
eV, Reference 10) contact on the front surface of an
MEH-PPV film which is deposited by spin-casting from
15   dilute tetrahydrofuran solution containing 1% MEH-PPV by
weight onto a glass substrate. The resulting MEH-PPV
films have uniform surfaces with thicknesses near 1200Å.
The glass substrate had been previously coated with a
layer of indium/tin-oxide to form an "ohmic" contact.
20   The Indium contact is deposited on top of the MEH-PPV
polymer film by vacuum evaporation at pressures below
4x10^{-7} Torr yielding active areas of 0.04 cm^2.
           While ramping the applied bias, yellow-orange
light becomes visible to the eye just below 9 V forward
25   bias (no light is observed under reversed bias). Above
15 V, the rectification ratio of the diode exceeds 10^4.
           The EL spectra, obtained with 3 V AC superposed
(at 681 Hz) on 13V forward bias, showed characteristic
spectral features similar to those observed in the
30   photoluminescence of MEH-PPV.[11] The room temperature
electroluminescence peaks near 2.1 eV with a hint of a
second peak above 1.9 eV. At 90K, the intensity
increases and shifts to the red, and the two peaks become
clearly resolved.

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The electroluminecence intensity was measured
as a function of current flow under increasing forward
bias. The quantum efficiency was determined with a
calibrated Silicon photodiode and corrected for the
5   spectral response and the solid angle of the collecting
optics. The measured quantum efficiency at 0.8 mA is
$\approx 5 \times 10^{-4}$ photons per electron for Indium electrodes.

Example 4

10   Light-emitting diodes (LEDs) were fabricated
consisting of a rectifying calcium (work function = 3 eV,
Reference 10) contact on the front surface of an MEH-PPV
film which is deposited by spin-casting from dilute
solution onto a glass substrate. The resulting MEH-PPV
15   films have uniform surfaces with thicknesses near 1200Å.
The glass substrate has been partially coated with a
layer of indium/tin-oxide to form an "ohmic" contact.
The calcium contact is deposited on top of the MEH-PPV
polymer film by vacuum evaporation at pressures below
20   4×10^{-7} Torr yielding active areas of 0.04 cm^2.
For the calcium/MEH-PPV diodes, rectification
ratios as high as 10^5 are achieved.
While ramping the applied bias, yellow-orange
light becomes visible to the eye just above 3 V forward
25   bias (no light is observed under reversed bias). The
quantum efficiency was determined with a calibrated
Silicon photodiode and corrected for the spectral
response and the solid angle of the collecting optics.
The measured quantum efficiency at 0.8 mA is $\approx 7 \times 10^{-3}$
30   photons per electron for calcium electrodes (i.e., nearly
1%!!). The emission from the Calcium/MEH-PPV LEDs is
bright and easily seen in a lighted room at 4V forward
bias.

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Example 5

Light-emitting diodes (LEDs) were fabricated
consisting of a rectifying calcium (work function = 3 eV,
Reference 10) contact on the front surface of an MEH-PPV
5 film which is deposited by spin-casting from dilute
solution onto a flexible transparent
polyethyleneterephthalate (PET) film (7 mils thickness)
as substrate. The resulting MEH-PPV films on PET have
uniform surfaces with thicknesses near 1200Å. The PET
10 substrate is pre-coated with a layer of indium/tin-oxide
to form an "ohmic" contact. The calcium rectifying
contact is deposited on top of the MEH-PPV polymer film
by vacuum evaporation at pressures below 4×10^{-7} Torr
yielding active areas of 0.04 cm^2.

15   For the calcium/MEH-PPV diodes, rectification
ratios as high as 10^3 are achieved.

While ramping the applied bias, yellow-orange
light becomes visible to the eye just above 9 V forward
bias (no light is observed under reversed bias). The
20 quantum efficiency was determined with a calibrated
Silicon photodiode and corrected for the spectral
response and the solid angle of the collecting optics.
The measured quantum efficiency at 5.5 μA is 4×10^{-3}
photons per electron for calcium electrodes. The
25 emission from the calcium/MEH-PPV LEDs is bright and
easily seen in a lighted room at 4V forward bias.

Example 6

MEH-PPV is cast onto a film of pure UHMW-PE
30 which has been stretched to a moderate draw ratio (e.g.
draw ratio >20, Reference 11). The MEH-PPV is observed
to orient spontaneously along the draw direction; both
the photo-absorption and the photoluminescence spectra
are highly anisotropic. Since the luminescence spectrum
35 is polarized with electric vector along the chain

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alignment direction, light-emitting diodes can be
fabricated which emit polarized light.

Example 7

5   · MEH-PPV was gel-processed and chain oriented as
a guest in UHMW-PE. The gel-processing of a conjugated
polymer as a guest in a gel-processed blend involves
three steps:
                A.   Co-solution with a suitable carrier polymer
10   B.   Carrier Structure Formation
                C. Drawing of the Carrier/Polymer blend.

Carrier Solution Preparation, Film Formation, Gelation,
and Drawing.

15   PE-MEH-PPV blends are prepared by mixing MEH-
PPV (M_w=450,000) in xylene with UHMW polyethylene
(Hostalen GUR 415; M_w=4x10^6) in xylene such that the PE
to solvent ratio was 0.75% by weight. This solution is
thoroughly mixed and allowed to equilibrate in a hot oil
20   bath at 126°C for one hour. The solution is then poured
onto a glass surface to cool, forming a gel which was
allowed to dry (into a film). Films were then cut into
strips and tensile-drawn over a hot pin at 110-120°C.
Once processed in this manner, the films are oriented.
25   The high work function and low work function electrodes
are offered as in Examples 4 and 5, and LEDs result.

30

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We claim:

1.   A process for fabrication of a light-
emitting diode which emit visible light, which process
5   comprises the steps of:
        i)   precoating a substrate with a transparent
conducting first layer, said first layer having high work
function and serving as an ohmic hole-injecting
electrode;
10   ii)   casting upon said first layer directly
from solution, a thin transparent layer of a soluble
conjugated polymer; and
        iii)   fabricating onto the conjugated polymer
film from a low work function metal, a negative,
15   electron-injecting contact, said electron-injecting
contact acting as the rectifying contact in the diode
structure.

        2.   The process of claim 1, wherein the
20   substrate is a rigid, transparent, inorganic substrate.

        3.   The process of claim 1, wherein the
substrate is a flexible, transparent, organic polymer
substrate.
25
        4.   The process of claim 1, wherein he
conducting first layer is an electronegative metal.

        5.   The process of claim 1, wherein the
30   conducting first layer is a conductive metal oxide.

        6.   The process of claim 1, wherein the
conjugated polymer film comprises poly(2-methoxy,5-(2'-
ethylhexyloxy)-1,4-phenylenevinylene), MEH-PPV.
35

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7.   The process of claim 1, wherein the low
work function metal is calcium.

8.   A light-emitting diode comprising a
5   substrate, a transparent conducting first layer, said
first layer deposited upon said substrate and having a
high work function and serving as a ohmic hole-injecting
electrode, a film of conjugated polymer present upon said
conducting first layer, said film of conjugated polymer
10   having been cast directly from solution as a thin,
transparent layer onto said first layer, and a negative,
electron-injecting contact fabricated onto said film of
said conjugated polymer, said contact being formed from a
low work function metal and acting as the rectifying
15   contact in the diode structure.

9.   The light-emitting diode of claim 8,
further characterized by emitting visible light and by
turning on at voltages below 5 volts.
20

10.   The light-emitting diode of claim 9,
wherein the substrate is a rigid, transparent, inorganic
substrate.

25   11.   The light-emitting diode of claim 8,
wherein the substrate is a flexible, transparent, organic
polymer substrate.

12.   The light-emitting diode of claim 8,
30   wherein the conducting first layer is an electronegative
metal.

13.   The light-emitting diode of claim 12,
wherein the electronegative metal comprises gold.
35

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14. The light-emitting diode of claim 8, wherein the conducting first layer is a conductive metal oxide.

15. The light-emitting diode of claim 8, wherein the conductive metal oxide is indium/tin oxide.

16. The light-emitting diode of claim 8, wherein the conjugated polymer film comprises MEH-PPV.

17. The light-emitting diode of claim 16, wherein the substrate is polyethyleneterephthalate.

18. The light-emitting diodes of claim 16 wherein the low work function metal is calcium.

19. The light-emitting diode of claim 16, wherein the substrate is an orientation-inducing substrate by which the MEH-PPV is chain-aligned and oriented thereupon, thus yielding a light-emitting diode which emits polarized light.

20. A process for fabrication of a light-emitting diode which emits visible light, which process comprises the steps of:
    i)   casting a free-standing, semitransparent film of a soluble conjugated polymer from solution, said film serving as a luminescent, semiconducting polymer and simultaneously as a substrate;
    ii) coating the free-standing, conjugated polymer film on one side with a transparent conducting first layer, said transparent conducting first layer having a high work function and serving as the ohmic hole-injecting electrode; and

-25-

iii) fabricating a negative electron-injecting contact onto the other side of the conjugated polymer film from a low work function metal, said contact acting as the rectifying contact in the diode structure.

5

21. The process of claim 20, wherein the conducting first layer is an electronegative metal.

22. The process of claim 20, wherein the
10   conducting first layer is a conductive metal oxide.

23. The process of claim 20, wherein the conjugated polymer film is poly(2-methoxy,5-(2'-ethylhexyloxy)-1,4-phenylenevinylene), MEH-PPV.

15

24. The process of claim 20, wherein the low work function metal is calcium.

25. A light-emitting diode comprising a free-
20   standing, semitransparent semiconducting film of a soluble conjugated polymer, said film having been cast directly from a solution of said polymer, said film serving as a luminescent, semiconducting polymer and simultaneously as a substrate; a transparent conducting
25   first layer coated upon one side of said free-standing, transparent film, said first layer having high work function and serving as an ohmic hold-injecting electrode, and a negative electron-injecting contact fabricated onto the other side of the conducting polymer
30   film, said contact formed from a low work function metal and acting as the rectifying contact in the diode structure.

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-26-

26. The light-emitting diode of claim 24,
further characterized by emitting visible light and by
turning on at voltages below 5 volts.

5   27. The light-emitting diode of claim 25,
wherein the conducting first layer is an electronegative
metal.

28. The light-emitting diode of claim 26,
10   wherein the electronegative metal is gold.

29. The light-emitting diode of claim 24,
wherein the conducting first layer is a conductive metal
oxide.
15

30. The light-emitting diode of claim 24,
wherein the conductive metal oxide is indium/tin oxide.

31. The light-emitting diode of claim 24,
20   wherein the conjugated polymer comprises MEH-PPV.

32   The light-emitting diode of claim 24
wherein the low work function metal is calcium.

25   33. A process for fabrication of a light-
emitting diode which emits polarized visible light, said
process comprising the steps:
          i)   gel-processing a soluble conjugated
polymer in admixture with an ultra-high molecular weight
30   carrier polymer, an oriented, free-standing film in which
the conjugated polymer is chain-aligned, said chain-
aligning resulting in polarized luminescence,
          ii) coating said oriented free-standing film
on one side with a transparent, conducting first layer,
35

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said first layer, having high work function and serving
as an ohmic hole-injecting electrode, and

　　　iii) fabricating a negative, electron-injecting
contact onto the other side of the oriented free-standing
5   film, said contact fabricated from a low work function
metal and acting as the rectifying contact in the diode
structure.

　　　34.　The process of claim 33, wherein the
10   carrier polymer is polyethylene.

　　　35.　The process of claim 33, wherein he
conducting first layer is an electronegative metal.

15   　　　36.　The process of claim 33, wherein the
conducting first layer is a conductive metal oxide.

　　　37.　The process of claim 33, wherein the
conjugated polymer is poly(2-methoxy,5-(2'-
20   ethylhexyloxy)-1,4-phenylenevinylene), MEH-PPV.

　　　38.　The process of claim 33 wherein the low
work function metal is calcium.

25   　　　39.　A light-emitting diode comprising an
oriented, free-standing film formed from a gel-process
admixture of soluble conjugated polymer with ultra-high
molecular weight carrier polymer in which the conjugated
polymer is chain-aligned, said chain-aligning resulting
30   in polarized luminescence, said film serving as a
luminescent, semiconducting polymer and simultaneously as
a substrate, a transparent, conducting, first layer
coated upon one side of said free-standing, transparent
film, said first layer, having high work function and
35   serving as an ohmic hold-injecting electrode and a

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negative electron-injecting contact fabricated onto the
other side of the semiconducting film, said contact
formed from a low work function metal and acting as the
rectifying contact in the diode structure.

5

40.   The light-emitting diode of claim 39,
further characterized by emitting visible light and by
turning on at voltages below 5 volts.

10   41.   The light-emitting diode of claim 39,
wherein the conducting first layer is an electronegative
metal.

42.   The light-emitting diode of claim 41,
15   wherein the electronegative metal is gold.

43.   The light-emitting diode of claim 39,
wherein the conducting first layer is a conductive metal
oxide.

20

44.   The light-emitting diode of claim 43,
wherein the conductive metal oxide is indium/tin oxide.

45.   The light-emitting diode of claim 39,
25   wherein the conjugated polymer film is MEH-PPV.

46.   The light-emitting diode of claim 45,
wherein the carrier polymer is polyethylene.

30   47.   The process of claim 39, wherein the low
work function metal is calcium.

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CHED 123

Comparison of poly(p-phenylene vinylene) and poly(p-phenylene vinylene) precursor derivatives

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Poly(p-phenylene vinylene)(PPV)and its derivatives are conducting polymers that are of interest for their various electrical and optoelectronic properties. These properties are due to their highly conjugated structure. Unfortunately, this structure also leads to their insolubility and difficulty in processing. PPV's are commonly synthesized from easily processible precursor polymers by way of a solid-state thermal elimination reaction. We are primarily interested in the qualitative and kinetic parameters of this synthetic route as they influence the properties of the resulting polymer. We have used thermogravimetric analysis, differential scanning calorimetry, and evolved gas analysis in our investigation of four different precursor PPV's. Poly(p-phenylene vinylene)(PPV) and poly(2,5-dimethoxy-phenylene vinylene)(DM-PPV) are synthesized by a xanthate precursor route. Poly(2,3-diphenyl-phenylene vinylene)(DP-PPV) and poly(phenoxy-phenylene vinylene)(PO-PPV) are synthesized by a chlorine precursor route. Some specific areas of our investigation include: the identification of reaction mechanisms, the comparison of precursor routes, and the accelerated lifetime testing of precursor polymers.
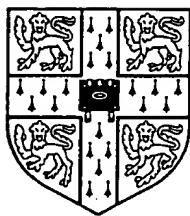
Short Lifetimes of Light Emitting Polymers

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Introduction

The following manuscript was submitted as part of the MPhil program in *Microelectronic Engineering and Semiconductor Physics* at the Microelectronics Research Centre (MRC) of the Cavendish Laboratory at the University of Cambridge. The manuscript is a literature survey undertaken by the author as part of the MESP program during Lent term 1997 and is the basis of a talk of the same title given at the MRC on January 20, 1997.

1 Basic Layout of Presentation

Before introducing the main topic of this paper— short lifetimes of light emitting polymers—a few introductory sections are provided for background considerations. Background materials include short introductions to polymers and electroluminescence in polymers, before mechanisms responsible for the short lifetimes of light emitting polymers and related issues are discussed.

This survey is intended to be comprehensive but by no means exhaustive. In the following sections, there are instances in which two or more sections share related information; to eliminate redundancy, an issue will be addressed in full in the section where it has most relevance and will only be briefly mentioned in any other relevant sections.

2 History of Light Emitting Polymers

2.1 Polymers

Much of the terminology we will encounter for polymers, also affectionately known as macromolecules, rose out of the combined *efforts* of organic chemists, who created them, and the physical chemists, who characterized their physical properties.

Polymers are chains of smaller molecular components, called monomers. As a simple example, the polymer polyethylene (PE) is constructed (or polymerized) from the precursor ethylene by breaking the double bond in the ethylene molecule, as shown successively in Figures 1 and 2 below.

Polymers exist in many varieties ranging from the very simple repeating patterns of chains of monomers, to the somewhat more sophisticated molecular patterns as found in copolymers— polymers composed of two or more chemically distinguishable monomers. Copolymers, in turn, can exist in many configurations, owing to the many ways the individual monomers can be ordered. There are block polymers, in which large sections are repeated along the polymer chain; graft polymers where another polymer is attached as a
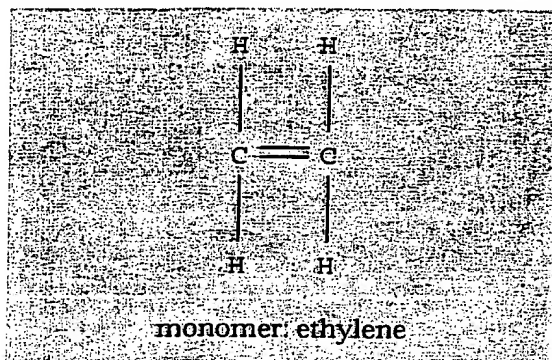
Figure 1: The *double-bonded* precursor to polyethylene: ethylene.
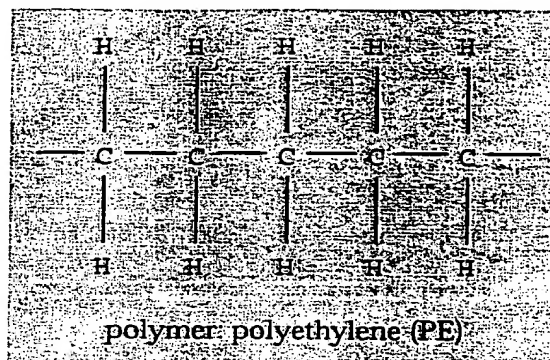
Figure 2: The single-bonded polymer polyethylene (PE).

side chain; random polymers where the different monomer units take on, as the name suggests, a random ordering to form the polymer chain; and so on.

Another important class of polymers is conjugated polymers. Conjugated polymers consist of carbon backbones with alternating single and double bonds and have shown great potential as light-emitting materials.

2.2 Light Emitting Polymers

The first organic electroluminescent devices [1][2] were discovered around the time the first light-emitting diodes (LEDs) were introduced into the commercial market in 1962. Like today, early devices were hampered by fabrication and packaging problems and short lifetimes [3].

Electroluminescence (EL) was first observed in conjugated polymers in 1990 by Burroughes *et al.* [4], which reveals the relative youth of this field. Evidence for electroluminescence from the seminal paper by Burroughes *et al.* is shown in Figure 3.

Prior to this, electroluminescence had been wit-nessed in organic molecules by Tang and Van Slyke in 1987 [5], who revived interest in organic EL. All of these were originally preceded by the work of Partridge in 1983 [6], whose work largely went unnoticed.

Since the advent of electroluminescent polymers, conjugated polymeric materials with emissions spanning the broad spectrum of visible [4][8][9][10][11][12][13] and non-visible radiation (near infrared [14]) have been fabricated, as shown in Figure 4. A voltage-tunable-luminescent device has been fabricated using poly(thiophene) blends [14][15]. One group [16] has created white-light devices by using appropriate combinations of these EL materials.

Many polymers are now known to display electroluminescence. Among the favorites are poly(phenylene vinylene) [PPV] (Figure 5), and variations on a theme, poly(2-methoxy-5(2'-ethyl)hexoxy-phenylene vinylene) [MEH-PPV] (Figure 6), [DP-PPV] (Figure 7), poly(2,5-bis(5,6-dihydrocholestan-oxy)-1,4-phenylene vinylene) [BCHA-PPV], and [CN-PPV], and a plethora of others including aluminum tris(8-oxyquinolinate) [Alq3], poly(2-dodecoxy-p-phenylene) [C12OPPP],

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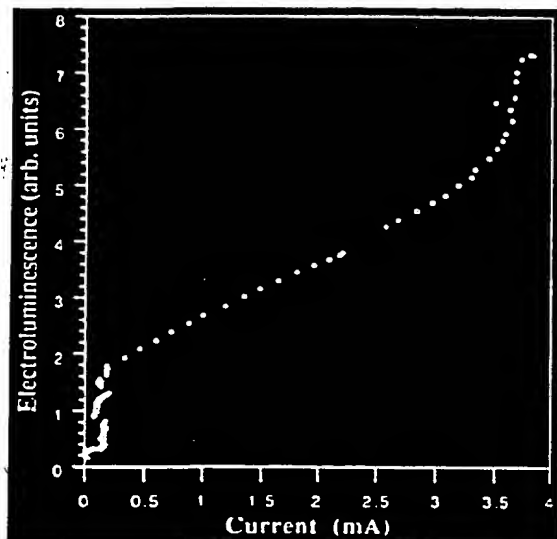
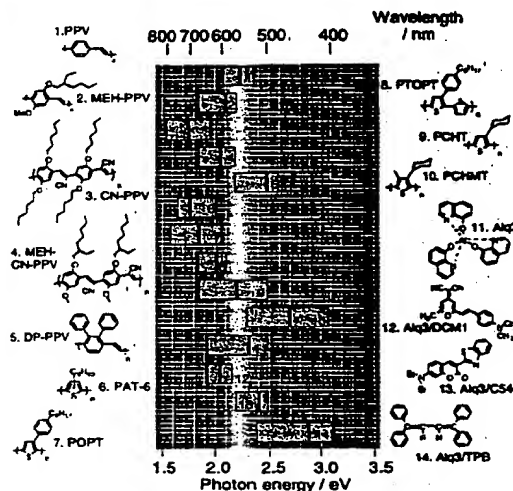Figure 3: Electroluminescence in PPV. From Burroughes et al. [4].

Figure 4: Polymeric materials with emissions spanning the broad spectrum of visible and non-visible radiation have been synthesized. From Gymer [7].

and poly(3-octylthiophene) [P3OT]. The chemical structures of many other EL polymers not already mentioned along with their full-width, half-maximum EL emission range can be found in Figure 4.

The similar electroluminescent (EL) and photoluminescent (PL) spectra of these materials [17][18][19][20][21] suggest that the same mechanisms are responsible for both phenomena, justifying, in many cases, why these terms are used interchangeably in the literature. In support of this assertion, an experiment by Tang and Van Slyke [5] has shown an increase in both EL and PL by fluorescent-dye doping of Alq$_3$-based devices.

2.3 Synthesis of Polymers

The synthesis of polymers is an important consideration in the fabrication of light emitting devices. The various properties of polymers, particularly solubility, limit the methods by which devices can be constructed. There are different routes to PPV from different precursors, as shown in Figures 8 and 9. For example, one synthesis of the insoluble conjugated polymer PPV is a two-step process: a precursor monomer is polymerized and forms a soluble precursor polymer, after which the precursor is spin-coated onto a substrate and thermally converted to PPV at a temperature ranging between 200°C to 300°C in a vacuum or inert (argon) atmosphere [22]. This can lead to the formation of hydroxyl groups [23] and carbonyl groups [24]—residues left over from the conversion process. The effects of carbonyl on the luminescence of devices is discussed in a later section.

Alkoxy-substituted derivatives of PPV, such as BCHA-PPV, are soluble in organic solvents which allows for casting of solid films [26].
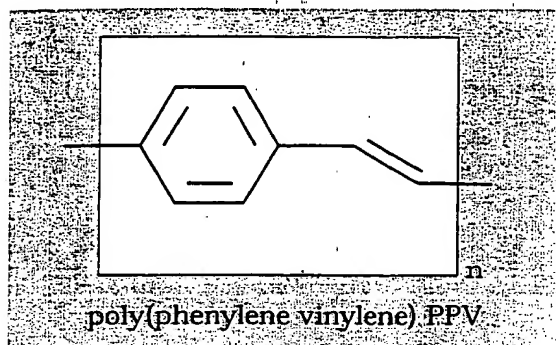
Figure 5: Monomer of the electroluminescent polymer poly(phenylene vinylene) [PPV].
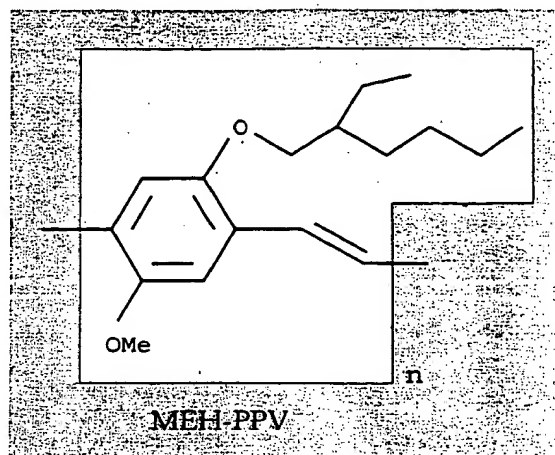

Figure 6: Monomer of the electroluminescent polymer poly(2-methoxy-5(2'-ethyl)hexoxy-phenylene vinylene) [MEH-PPV].

Purity in polymeric materials, although not as significant as in inorganic materials like crystalline semiconductors, is becoming more of a concern; Sheats et al. [3] have reported that the lifetime of a TPD/Alq$_3$ device (where Alq$_3$ was co-evaporated with 0.5 wt% quinacridone of 98% nominal purity) exhibited a lifetime factor 10^{-4} less than a similar device where the quinacridone was purified by a sublimation technique.

2.4 Utilizing Light Emitting Polymers

Organic light emitting diodes (OLEDs) may be utilized for many purposes ranging from replacing standard light emitting diodes (LEDs), to flat panel displays, and flexible displays [18] for niche applications. Devices have exhibited high resolution, fast switching, and fast emission [7]. They also tend to activate at voltages as low as 3 Volts and tend to operate below 10 Volts [27]. They are also light-weight relative to the existing technology.

However, even with these laudable attributes, the following factors are preventing this new technology from dominating the competing technologies at this

time: the processes by which polymers are synthesized and processed, as discussed earlier, and device degradation once the device has been fabricated. Among other problems cited is the need to improve luminous efficiency and color gamut [27] (see Figure 10). In this paper, we will concentrate mainly on the problems of device lifetimes and degradation, and some related peripheral issues.

3 The Physics of Light Emitting Polymers

3.1 Electroluminescence

In the seminal paper by Burroughes et al. [4], electroluminescence—in this case emission of yellow-green light—was induced by applying a voltage across a layer of poly(phenylene vinylene) [PPV]. Since that time, electroluminescence has been observed in many other polymers [28][29].

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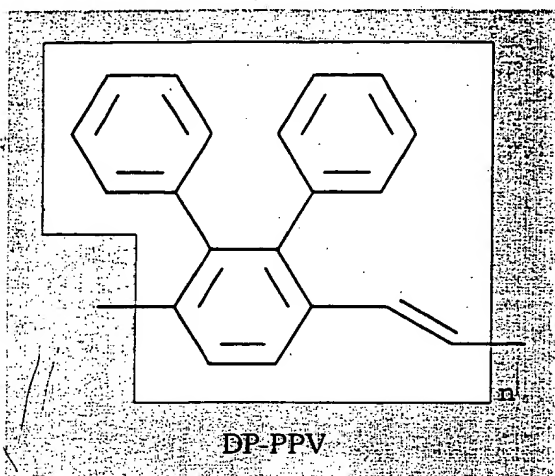
Figure 7: Monomer of the electroluminescent polymer DP-PPV.
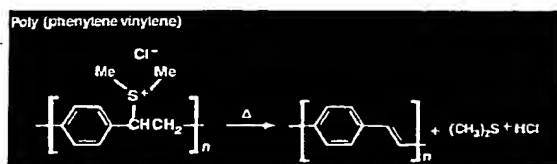
Figure 8: Soluble precursor synthetic route for poly(phenylene vinylene) [PPV]. From Reynolds [25].
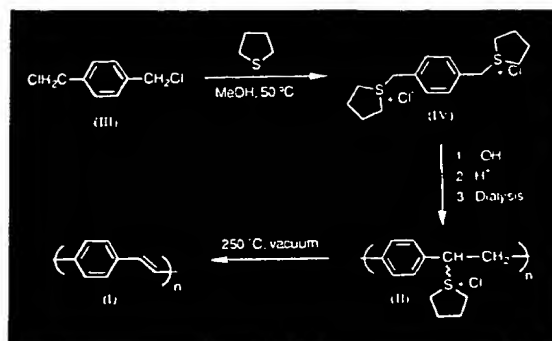

Figure 9: Synthetic route to PPV. From Burroughes et al. [4].
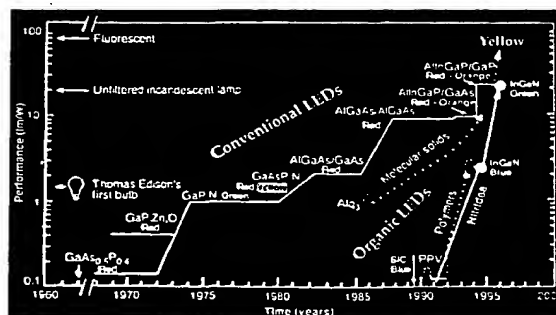
Figure 10: Progress in LED efficiency. Adapted from Sheats et al. [3].

Electroluminescence is brought about by injecting electrons and holes from opposite sides of the conjugated polymer which then recombine in the polymer to form self-localized excited states that decay radiatively [4] (see Figure 11).

It is preferable to asymmetrically inject electrons via a low work-function cathode (approximately 3–4 eV [3]) and holes via a transparent, high work-function anode [27][21] (approximately 5 eV [3]). The conjugated polymer layer sandwiched between the two electrodes acts as a recombination cen-

ter and must exhibit efficient luminescence, charge transport, and efficient charge transfers with both electrodes [3] (see Figure 12). Indium-tin-oxide (ITO) has become the *de facto* anode material.

The inherent asymmetry built into these devices leads to some current rectification, and hence these devices are usually referred to as light emitting diodes (LEDs), although Jeglinski et al. reported electrical and electroluminescent symmetric behavior in a light emitting diode utilizing poly(phenylene acetylene) [PPA] as the electrolumines-
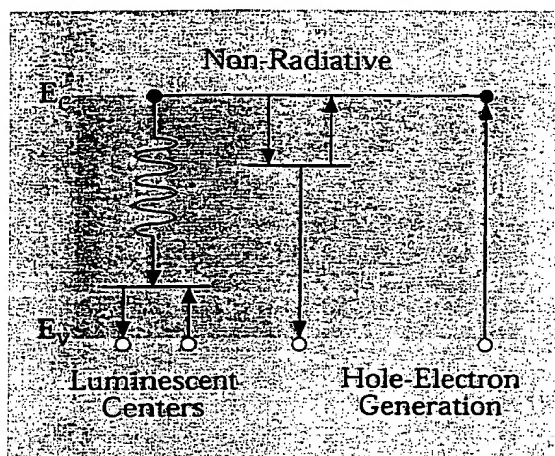
Figure 11: Electroluminescence is brought about by recombining electrons and holes in the bulk polymer. Not all electrons and holes will *recombine*, due to various non-radiative traps or quenching sites inside the polymer, like carbonyl groups formed by photo-oxidation. Adapted from Ivey [30].

cent polymer [31].

Excitation is achieved mainly along conjugation lengths consisting of 10 to 15 monomers [3]. In PPV, for example, the excitation moves directly to a non-radiative interchain exciton, although reversions to the radiative intrachain excitations are possible [32]. Charges move along the polymer by electron transfer reactions [33] (hopping) between polymer molecules. In polymers which exhibit the structural symmetry of PPV, these excitations exist in three varieties: (uncharged) polarons (polaron excitons), singly charged polarons, and doubly charged polarons (bipolarons) [4][34][35] (see Figure 13). Interchain transport is thought to be far less efficient than tunneling through σ bonds [36][37]. Mobilities of holes in polymers tend to be in the range of 10^{-4} cm^2/Vs and 10^{-8} cm^2/Vs;
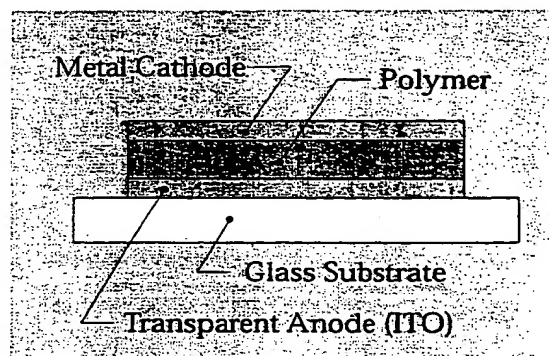
Figure 12: In a typical single-layer device, the electrons are injected into the polymer from a low work-function metal cathode and holes are injected into the polymer from a high work-function transparent anode. In the applied electric field, the electrons and holes recombine in the bulk polymer and form excited states which decay radiatively.

electron mobilities are even lower, thought to be due, in part, to trapping sites containing oxygen [38].

4 Device Degradation and Lifetimes

Lifetimes for OLEDs have been reported near 5,000 hours for the best light-emitting polymers [40], but most devices don't operate near this figure (see Figure 14). Light emitting polymer devices exhibit short lifetimes for various reasons; among the various direct and indirect issues cited in the literature are: photo-oxidation, singlet oxygen, *dark spots*, reactive metal contacts, problems in injection of electrons and holes, quantum efficiency, recombination efficiency, barrier height between hole transport layer (HTL) and ITO [41], recrystalliza-
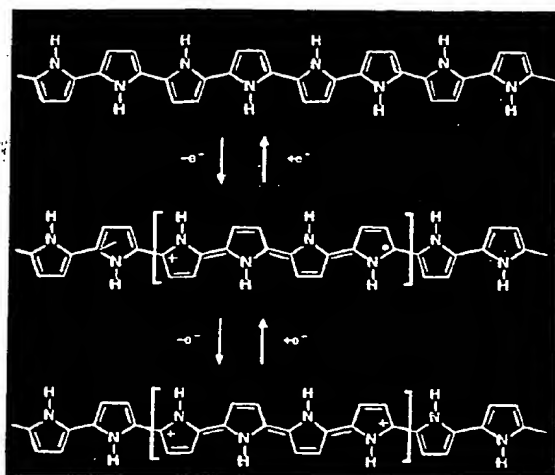
Figure 13: Oxidation and reduction (doping): charge carrier formation, polaron (-e$^-$) and bipolaron (-2e$^-$), in polypyrrole. Adapted from Reynolds [25].
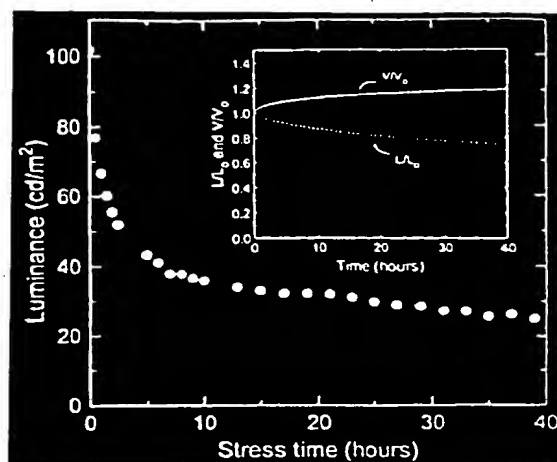

Figure 14: Degradation of luminance vs. time for biased device. Inset shows evolution of luminance and applied voltage for constant-current stressed device. From McElvain *et al.* [39].

tion of HTL [42], interdiffusion across organic layers [43], device configuration [41], deterioration of electrode layers [44], luminance decay rate directly proportional to injection current density [45], cumulative and irreversible coulombic degradation [45], and many others. Few of the cited issues above will not be addressed further as they are not the dominant degradation mechanisms in light emitting polymers.

In order to systematically address the synergistic issues, we will deal with each issue on an individual basis. Since device degradation can take place in any of the three layers of the usual single-layer devices; i.e., the metal cathode, the transparent anode, and also within the polymer itself, the following sections will be organized as follows:

5 Polymer-Related

   5.1 Photo-Oxidation

   5.2 Singlet Oxygen and Chain Scissions

   5.3 Carbonyl Groups and Other Destructive Species

   5.4 Oxygen Migration from ITO Anode and Micro-shorts

   5.5 Recrystallization and Other Structural Changes

   5.6 Quantum Efficiency

6 Cathode-Related

   6.1 *Dark Spots*

   6.2 Reactive Metal Contacts

   6.3 Electromigration-Induced Diffusion

   6.4 Electron Injection

7 Anode-Related

   7.1 Oxygen Migration from ITO

5 Polymer-Related

5.1 Photo-Oxidation

The lifetimes of devices is severely compromised if they are operated in an oxygen atmosphere. This instability in air was originally witnessed in early electron conduction experiments with aromatic hydrocarbon polymers [25].

Welch *et al.* [46] concluded that photo-oxidation, also referred to as photodegradation, is related to the functionalities present on the polymer, catalytic effects of the substrate, itself a function of the electronic configuration, and UV exposure conditions.
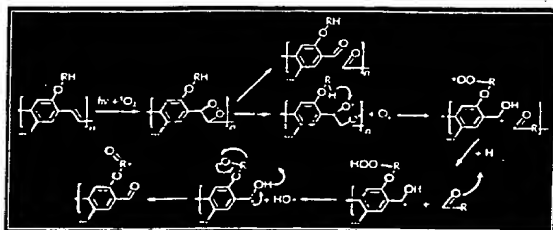
Figure 15: Oxidation mechanism for alkoxy-substituted PPV derivatives showing formation of esters, aromatic aldehydes, and alcohols. From Cumpston and Jensen [47].

Yan *et al.* [48] have shown that the intensity of PPV emission is greatly reduced if luminescence experiments are carried out in an oxygen atmosphere rather than a nitrogen atmosphere. There is much evidence suggesting that device lifetimes are longer in nitrogen atmospheres [49][50]. This suggests

that reactions involving oxygen are one facet of device degradation. Inhibitors of photo-degradation can come in many varieties, ranging from chain-breaking acceptors, chain-breaking donors, UV absorbers, metal deactivators, stoichiometric and catalytic peroxide decomposers, and excited state-quenchers. UV absorbers, for example, work by absorbing radiation and converting it to thermal energy [51]. Chromophores, the absorbers of light in the polymers, redirect the excitation energy to quenchers that help convert the absorbed energy to vibrational energy. Peroxide decomposers help decompose peroxides to alcohols.

According to Faucitano *et al.* [51], photo-oxidation and photothermal oxidation are complex free-radical processes strongly dependent on the chemical nature of the polymer. Chemical stabilizers against various photo-oxidative mechanisms have been developed, but must be tailored for each specific polymer. The photo-oxidative mechanisms create a plethora of functional groups such as carbonyls, acids, esters, and alcohols (see Figures 15 and 16), along with unsaturation, chain scissions, and crosslinks. The complete loss of mechanical properties of polypropylene (PP) can be triggered by one oxidized carbon atom per 200 atoms. The oxidation leads to polar functional groups which further deteriorate other properties of the polymers including dielectric properties, transparency, and hydro-repellence. Residual catalysts, used in the fabrication of polymers, have also been shown to be contributors to photo-oxidation.

5.2 Singlet Oxygen and Chain Scissions

Singlet oxygen has been cited as a major contributor to photo-oxidation [52]. These reactions, characterized by very low activation energies, are a re-
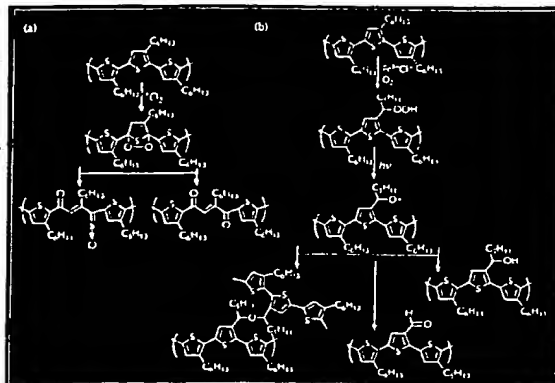
Figure 16: Singlet oxygen (a) and free-radical degradation (b) of P3HT. From Cumpston and Jensen [47].

sult of the interaction between radicals on the polymer's oxygen's unpaired electrons when oxygen is in the ground state.

Singlet molecular oxygen ($a^1\Delta_g$) gives rise to chain scissions in BCHA-PPV [26]. The same group reports that singlet oxygen does not appreciably react with stilbene, the monomer analogue for the BCHA-PPV system. Photochemical absorption may also induce cis-trans isomerization of vinylene moieties and, as is the case in stilbenes—cyclization [53]. Gibson and Pochan suggested in 1982 that singlet oxygen led to the degradation of polyacetylene [54]. Holdcroft *et al.* [55][56] reported that singlet oxygen reacts with the poly(3-alkylthiophenes).

It has been shown that the free electrons of oxygen in polymers containing oxygen reduce the amount of conjugation. According to Scott *et al.*, the reduction in conjugation does not manifest itself in a spectral change; the expected blueshift is mitigated by the creation of quenching centers.

5.3 Carbonyl Groups and Other Destructive Species

A significant residual of the thermal conversion of a precursor into the polymer PPV is the aromatic aldehyde carbonyl moiety. It has been shown [22] that the carbonyl content (not present in the precursor) reduces luminescence of such devices, as shown in the Figure 17. Carbonyl formation and subsequent decrease of fluorescence has been witnessed in the UV irradiation of a PPV precursor [57]. Papadimitrakopoulos [22] also report that trace amounts of oxygen and prolonged exposure of the polymer to elevated temperatures creates carbonyl moieties and reduces luminescence.
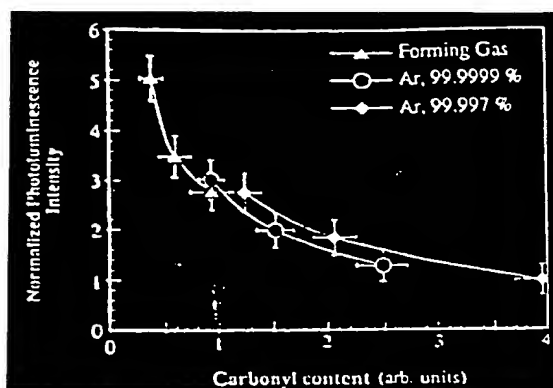

Figure 17: Effect of carbonyl content on the photoluminescence of PPV films. From Papadimitrakopoulos *et al.* [22].

Welch *et al.* [46] concluded that the formation of carbonyl groups during photodegradation was dominant in the presence of the metals Al and Au as electrodes. In non-oxidative conditions, there occurred no formation of carbonyl groups, however, in the case of Cu, the photodegradation of the polymers in oxidative and non-oxidative conditions was

still substantial, although the latter was 4.5 times as slow. To combat this problem of carbonyl formation, Papadimitrakopoulos *et al.* [22] has reported that the thermal conversion of the PPV precursor in a reducing atmosphere consisting of 15% hydrogen in nitrogen substantially reduced the amount of carbonyl moieties.

5.4 Oxygen Migration from ITO Anode and Micro-shorts

Scott *et al.* [27] report the oxidation of MEH-PPV using a Ca cathode and ITO anode, suspecting the migration of oxygen out from the ITO anode, which ultimately led to the quenching of luminescence and increase in device impedance. They also report the existence of microscopic shorts (in the end stages of operation) through the polymer which eventually reduce the active area of the LED and lead to thermal runaway. It has been recommended that a less conductive and less transparent layer between the polymer and the anode be used to prevent oxygen migration; those who have used a polyaniline layer have demonstrated improved behavior [18][58]. It is conjectured that the microshorts are due to electrode surface roughness, particulate contamination, and inhomogeneities within the polymer.

Devices that are encapsulated exhibit much longer lifetimes than unencapsulated devices, as shown in Figure 18. Encapsulated devices eliminate any external sources of oxygen, but not necessarily any internal oxygen sources like an ITO anode.

5.5 Recrystallization and Other Structural Changes

Operating temperatures have an effect on the spectral output of devices, as shown in Figure 19. Excessive heating of the polymer can cause problems
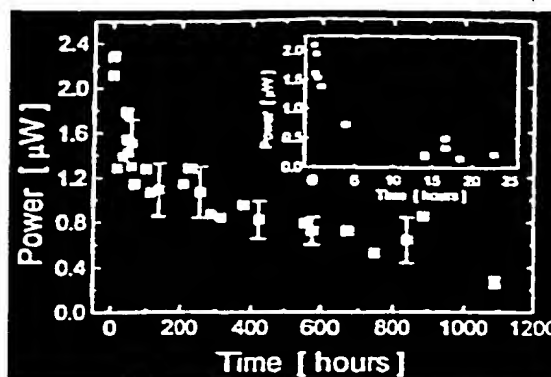

Figure 18: Luminance statistics of encapsulated OLEDs. Inset is statistics for unencapsulated devices. From Burrows *et al.* [44].

as well; although some light emitting polymers that are sublimated exhibit very good efficiencies, and have been tuned for specific emissive wavelengths, these devices have exhibited problems in device performance stability due to recrystallization and other structural changes [4].

5.6 Quantum Efficiency

The internal quantum efficiencies, defined as the number of photons emitted for the number of electrons injected, have increased in the last few years. Early device efficiencies ranged at about 0.1%, but have recently been brought into the 1% range. Quantum efficiencies as high as 4% have also been reported [21]. A 4% quantum efficiency means that the radiant (or luminous) efficiency, a function of driving voltage, refractice index, and other factors [59], is only around 0.25% [27].

Device efficiencies of 0.05% [4] and quantum efficiencies of 0.01% photons/electron [60] for ITO/PPV/Ca and ITO/PPV/Al devices have been reported [22]. The introduction of an electron
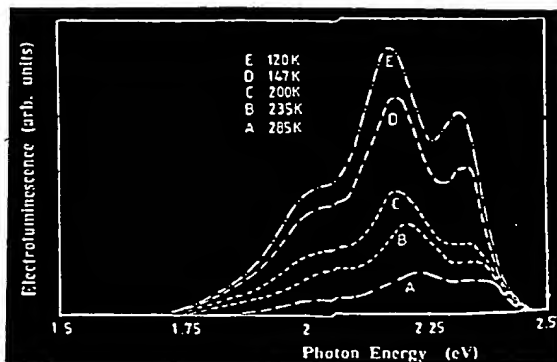
10

Figure 19: Thermal effects on the electrolumines-
cent spectrum of PPV. Adapted from Burroughes
et al. [4].

transport layer (see Figure 27) to ITO/PPV/Ca
single layer devices has brought the efficiency up to
0.8% [19].

6   Cathode-Related

6.1   "Dark Spots"

Some early fabricated devices exhibited *dark spots*
which were thought to be due to nonuniformities
of the layers, in particular, the metal electron-
injecting electrode. These *dark spots* would invari-
ably be non-emissive areas of the device and usu-
ally increased the impedance [27] of the devices.
Others attributed the *dark spots* to chemical reac-
tions taking place at the polymer/metal interface.
Recently, the use of less reactive metals for the
electron-injecting layer [61] with the introduction
of a charge transporting layer [62], specifically an
electron transport layer, has mitigated these prob-
lems. Electrochemical cells, which facilitate oper-
ation at lower voltages, used in conjunction with
less reactive metals for charge-injecting electrodes,
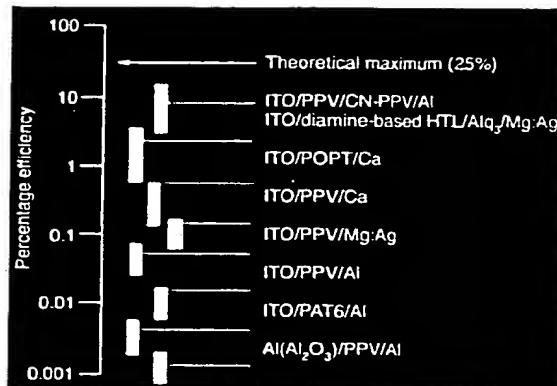
Figure 20: Quantum efficiencies of various elec-
troluminescent anode/polymer/cathode configura-
tions. Adapted from Gymer [7].

seem to have eliminated this particular problem
[13]. Device failure of early electroluminescent de-
vices was originally attributed to Joule heating at
the metal/polymer interface [4].

Recent experiments have shown that *dark spots*
may be due to water-induced delamination [39].

6.2   Reactive Metal Contacts

Device performance may also be hampered by
the migration of impurities [63] and dopants [64].
Welch *et al.* have studied the effect of metal sub-
strates on the photodegradation of polymers [46];
they conclude that aluminum causes more pho-
todegradation on the polymers polyvinyl flouride
[PVF] and polyacrylonitrile [PAN] than do the
other metals they studied, namely copper (Cu), sil-
ver (Ag), and gold (Au). They concluded that for
PAN, the hierarchy of degradation under oxidative
conditions was the following: Cu/PAN $\gg$ PAN $\gg$
Al/PAN $>$ Au/PAN $>$ Ag/PAN.

The formation of carbonyl groups during pho-
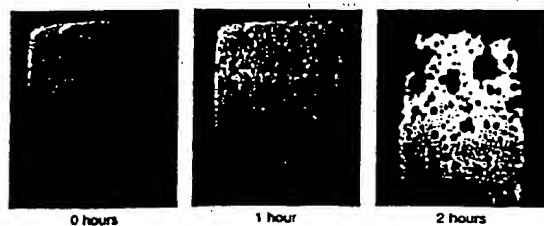todegradation was dominant in the presence of the

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Figure 21: Degradation of device: EL in an ITO/TPD/Alq$_3$ plus quinacridone/Mg device operated in N$_2$. Note formation of circular *dark spots*. These *dark spots* grow only in the presence of H$_2$O but not in N$_2$, negligibly in O$_2$, and independent of operation. Experiments show that *dark spots* are regions of water-induced delamination. From Sheats *et al.* [3].

metals Al and Au. In non-oxidative conditions, there occurred no formation of carbonyl groups, however, in the case of Cu, the photodegradation of the polymers in oxidative and non-oxidative conditions was still substantial, as mentioned earlier. The high heat capacities of the metals has been ruled out as a contributing factor responsible for the photodegradation of the EL polymer.

Scott *et al.* [27] report the degradation of Ca/Al cathodes, as shown in Figure 22.

6.3 Electromigration-Induced Diffusion

Cumpston and Jensen [65] report that the degradation of Al cathodes (see Figures 23 and 24) is due to the electromigration-induced diffusion of aluminum, which creates the non-emissive *dark spots*. According to their observations, the cathode defects occurred only in the active regions of the device and not in regions where there was no opposing ITO, which suggest that high current density-based
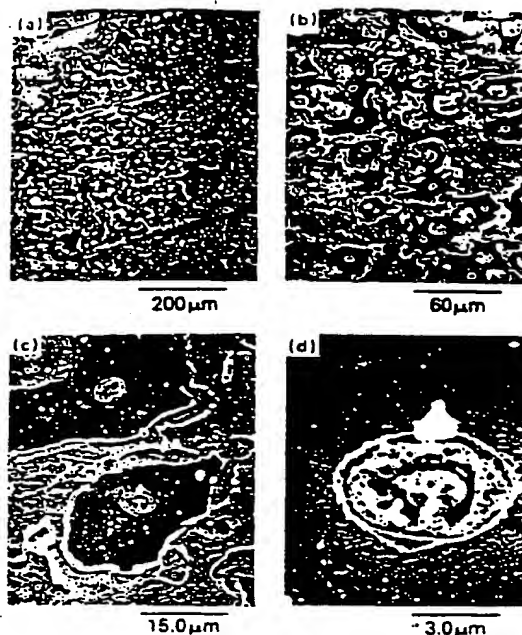

Figure 22: SEM images of degradation of Ca/Al cathode after complete device failure. From Scott *et al.* [27].

mechanisms are at work here. These effects may be due, in part, to the original morphology between the conjugated polymer film and Al cathode and are exacerbated by high currents and high temperatures. Fou and Rubner [66] report that polymers derived by chemical self-assembly do not exhibit *dark spots*. To reduce the electromigration-induced diffusion, it has been suggested that an overlying layer of metal can prevent the creation of island-morphology *dark spots*. Such Ag or Al [67] layers have been used to protect low work-function metals such as Mg or Ca [27][44].

Aziz and Xu [68] report that the formation of microscopic spots which create high current paths because of high electric fields which owe their exis-

tence to defects and edges in the cathode/polymer interface.

Do *et al.* [69] report the degradation of Al cathodes in an ITO/TPD/Alq3/-Al device. Aluminum was used because of its higher stability than MgAg. The size of the *dark spots* was in direct relation to the applied voltage. Material movement from the edges was particularly noticeable. Significant evidence for cathode degradation suggests that *dark spots* were almost entirely composed of the transparent aluminum oxide Al_2O_3, same as the expected top layer ($< 100 \mathring{A}$) of the Al electrode. The *dark spots* were also thought to occur in regions overlying heat and/or gas evolution and crevasse formation in the underlying EL organic layers.

Also, it was noticed that the longer the devices were placed in storage, the lower the EL intensity was found to be; this is attributed to crystallization of the TPD layer and slow oxidation of organic layers and Al cathode layers.

In a later paper by Do *et al.* [70], experiments further support the idea that the morphology of the Al cathode surface is related to deformations of the organic EL layer underneath, specifically gaseous evolution of oxygen and hydrogen thought to be a result of electrolysis of H_2O in the device.

6.4 Electron Injection

Electron injection takes place at the metal cathode/polymer interface. The metal should be a low work function metal, i.e., calcium and magnesium; however, these metals are very reactive and can contribute to device breakdown. Recent advances have added a charge transporting layer [62] (see Figure 27) between the electrodes and the polymer (see Reactive Metal Contacts). Introduction of these transport layers has led to an optimization of light output for selected wavelengths of emitted light [71].

More efficient injection contacts have been used to improve device performance [72][73]. Cathode materials being used are Al ($\Phi_w = 4.3eV$), Ag ($\Phi_w = 4.3eV$), In ($\Phi_w = 4.1eV$), Mg ($\Phi_w = 3.7eV$), Ca ($\Phi_w = 2.9eV$), ZrC ($\Phi_w = 3.6eV$) [74], and others. Anode materials are usually ITO ($\Phi_w \approx 4.7eV$) or Au ($\Phi_w = 5.1eV$). It has been noted that Al forms covalent bonds with the polymer and Ca forms ionic Ca and bipolarons [3]. Mg is thought to interact weakly and ZrC is stable in air. Electrodes of aluminum and silver/magnesium alloys are also being employed [7].

Van Slyke *et al.* [45] report that the luminance decay rate is directly proportional to injection current density, meaning that this coulombic degradation is cumulative and may be irreversible; however, it has been proposed that an AC bias current would prevent the formation of trapped space charges in the organic layers. This is interesting in light of the result advanced by Jeglinski *et al.* [31] regarding the symmetrically electric and luminescent behavior of PPA.

7 Anode-Related

Anode materials are usually a transparent, high work-function metal such ITO ($\Phi_w \approx 4.7eV$) or Au ($\Phi_w = 5.1eV$). There are problems associated with migration of oxygen and indium from the anode, as explained in the following sections.

7.1 Oxygen Migration from ITO

Scott *et al.* [27] report the oxidation of poly(2-methoxy-5(2'-ethyl)hexoxy-phenylenevinylene [MEH-PPV] using a Ca cathode and ITO anode, suspecting the migration of oxygen out from the ITO anode, which ultimately led to the quenching
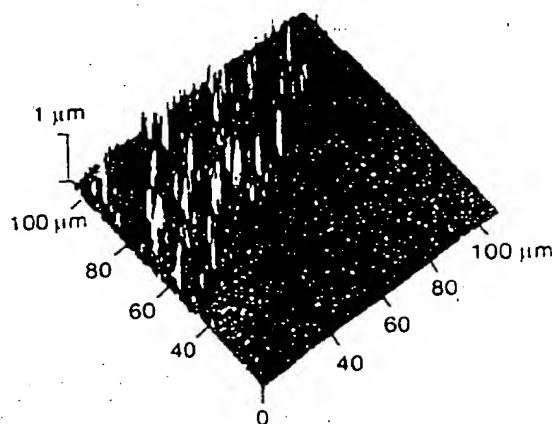
Figure 23: Atomic force micrograph of dark spot and neighboring pristine aluminum. From Cumpston and Jensen [65].
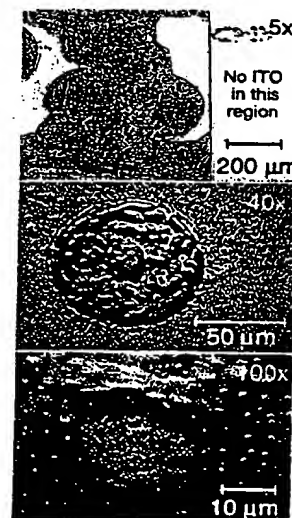
of luminescence and increase in device impedance. This effect obviously degrades both the polymer and the anode.

7.2 Indium-Tin-Oxide Damage

Chao et al. [75] report damage of ITO anodes, especially at high electric field strengths (see Figures 25 and 26). This damage manifests itself in volcano-like structures similar to those caused by electromigration-induced Al diffusion in Al cathodes, as described by Cumpston and Jensen [65]. Chao et al. suspect the high electric fields and Joule heating as the cause of these morphologies, whose depth ranges between 40 nm and 60 nm. The electrical resistance of the same ITO increases by 3 or 4 orders of magnitude from the original ITO samples.

Figure 24: Optical micrograph showing dark spot formation. From Cumpston and Jensen [65].

7.3 Indium Migration from ITO and Indium Contamination of EL Polymer

Esselink and Hadziioannou [76] and others [69] cite that the mechanical and thermal stability of polymer/electrode interfaces plays an important part in determining the lifetime of a device. They report that indium forms small granules of 30 nm width which form larger clusters. Because of an annealing procedure, it was found that indium had diffused through the anode/polymer interface into the polymer poly(3-octylthiophene) (P3OT); in a similar experiment, no diffusion of Al into the P3OT layer from the Al cathode was evidenced. Similarly, Schlatmann et al. [77] report indium contamination of the polymer, but, unlike Esselink and Hadziioannou, also report the contamination of the sequenced conjugated block
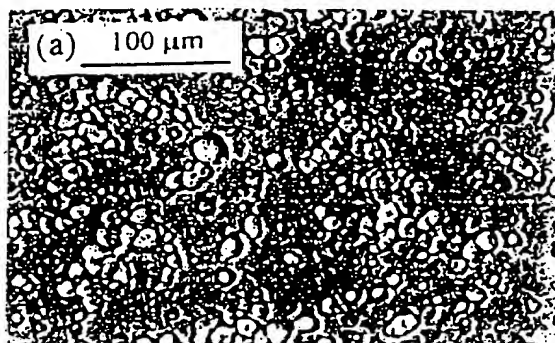
Figure 25: Morphology of ITO surface of damaged ITO/C12OPPP/Ca/Ag device as viewed from ITO side. From Chao *et al.* [75].

copolymer poly[dimethylsilyene-p-phenylene-vinylene-(2,5,5,2",5"-tetrabutoxy-p-terph-enyl-4,4'-ylene)-vinylene-p-phenylene] [Si-*p*PV1] by aluminum from the cathode.

Aziz and Xu [68] report infinite resistance of the ITO in failed devices and that indium (In) concentrations in the ITO had decreased. In their experiments, both aluminum and indium concentrations in the electrodes were reduced when compared to the background matrix of the cathode and anode, respectively. Aziz and Xu further report experiments suggesting that this outflux of electrode material is not due to local heating at temperatures which exceeded the degradation temperature of the polymer PPV. This anodic and cathodic corrosion is synergistic and was reported to also hold true for other anode/cathode materials including Mg and Au, respectively. Thus, Aziz and Xu propose an electrochemical mechanism for electrode degradation. It is suggested that the ionic conductivity of the PPV layer is enhanced by moisture and other impurities.

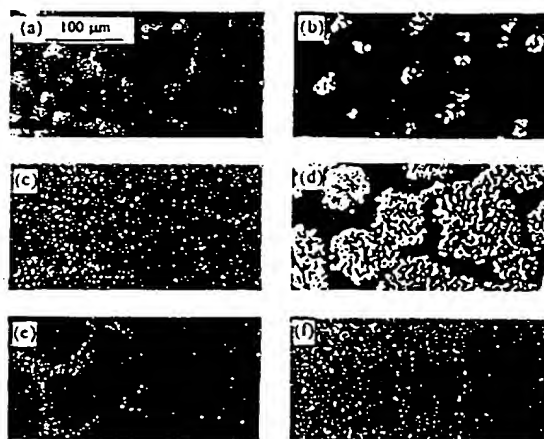Gautier *et al.* [78] report a modification to the

Figure 26: Morphology of poly(isobutylene) [PB] film coated on ITO surfaces for various voltages. From Chao *et al.* [75].

polymer/ITO interface consisting of a 35 Å layer, whose density is intermediate of the interfacing layers. This further supports the transport of oxygen into the polymer from the ITO.

8 Charge Transport Layer-Related

Single layer devices have been modified by the introduction of electron and hole transport layers (see Figure 27). Single layer devices create unbalanced charge injection which have the effect of reducing the recombination efficiency [3], thus charge transport (or injection) layers may be used for the anode or cathode or both. A new electroluminescent configuration utilizing a doped-hole transport layer as the emitter demonstrated an improved stability and a half-life of 3600 hours [79].

Van Slyke *et al.* [45] report highly stable electroluminescent Alq-based devices which includes
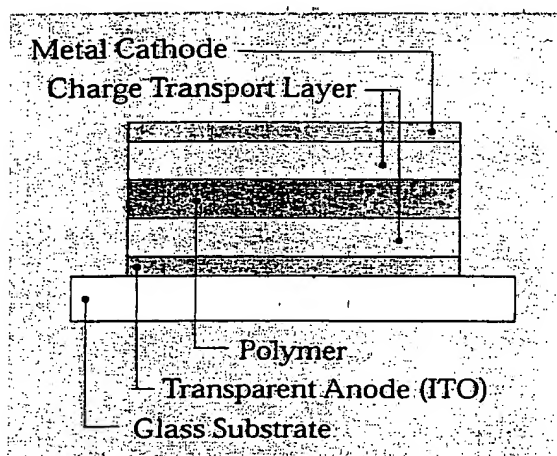
15

Figure 27: Modified devices utilize charge transport layers between the cathode/polymer and anode/polymer interfaces to increase electron and hole injection, respectively.

a CuPc stabilized hole-injecting contact and a hole-transport diamine layer using a naphthyl-substituted benzidine derivative; they also incorporated an alternating current which drives the device, as opposed to a direct current activation. The i-Si/ITO/CuPc/NPB/Alq/Mg:Ag device was reported to have a half-life of 4000 hours and an initial luminance of 510 cd/m^2. However, the hole-transporting layer was reported to have a low thermal tolerance. Hole transport layers include polymers such as N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine [TPD] and poly(9-vinylcarbazole) [PVK]. Adachi et al. [41] noted that device stability relates inversely with the barrier energy of the hole-injecting contact.

Although charge transport layers have been introduced to increase electron and hole injection, it seems that these novel approaches and variations to

single layer devices are not without problems. Interdiffusion of charge transport layers has been reported by Fujihira et al. [43]. In their observations, TPD and Alq3 diffused into each respective layer during heating. The poor thermal stability of TPD is also thought to cause crystallization [42][80].

Conclusion

This literature survey explored the many facets of device degradation and the mechanisms responsible for the short lifetimes of light emitting polymers. Among the mechanisms cited for the degradation of polymers was singlet oxygen, photo-oxidation, formation of carbonyl groups and other optically quenching chemical species, chemical artifacts of polymer synthesis, chain scissions, and indium contamination; among the mechanisms discussed for cathode degradation were *dark spots* thought to be a result of delamination due to water vapor, electromigration-induced diffusion of cathode metals, morphology of polymer/cathode interface, Joule heating, metal reactivity, and/or metal heat capacities; among the mechanisms cited for anode degradation were oxygen and indium migration out of ITO and into EL polymer; and the crystallization and diffusion of charge transport layers.

Disclaimer

Although the nature of this review focuses on the negative aspects of this nascent field, it is the author's sincere wish that they are not viewed as such. These aspects of device degradation merely demonstrate the exciting challenges that lie ahead for those who labor in this field and the knowledge of material properties, and the physical processes that govern them, that is to be derived from their

work.

Acknowledgements

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IN THE US PATENT AND TRADEMARK OFFICE
DECLARATION - US PATENT APPLICATION NO. 09/529,873
CAMBRIDGE DISPLAY TECHNOLOGY LIMITED

I, Professor Andrew Holmes declare and say as follows.

1. I am Professor Andrew Holmes of 19 Newton Road, Cambridge CB2 2AL, United Kingdom.

2. I received a Ph.D in April 1971 for research in the field of organic chemistry carried out at the University of London. I took up a postdoctoral position with Professor A. Eschenmoser at E.T.H. Zurich until October 1972. I held the position of Assistant Lecturer from 1972 to 1977 and then Lecturer from 1977 to 1994 in the Department of Chemistry at the University of Cambridge. I became the Director of the Melville Laboratory for Polymer Synthesis in October 1994. Since October 1998, I have held the title of Professor of Organic and Polymer Chemistry and was elected a Fellow of the Royal Society in May 2000.

3. I have read and am familiar with the documents referred to as "Antoniadis", "Wan", and "Hsieh" in the detailed action of the USPTO Office Action dated 24th December 2002.

4. Each of these documents discloses DP-PPV which is a polyphenylene vinylene derivative. Polyphenylene vinylene (PPV) has the structure:
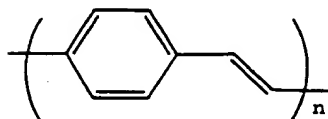
5. PPV is an **insoluble** conjugated polymer, i.e. it is not soluble in any solvent.

6. In order for a derivative of insoluble PPV to be rendered soluble, the PPV-derivative must have solubilising groups, which enable the polymer to be dissolved and to be solution processible. A solubilising group could be included in a further repeat unit or as a substituent on the phenylene ring of PPV, for example.

7. The structure of DP-PPV is:
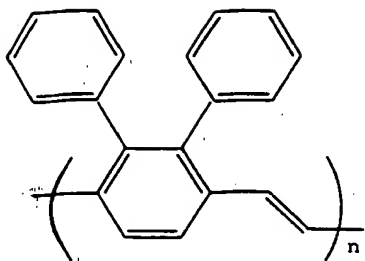
8.   DP-PPV has two adjacent phenyl substituents on the phenylene ring of the phenylene vinylene repeat unit. DP-PPV is **insoluble** which indicates that the phenyl **substituents** do not aid solubility of this polymer.

9.   I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true.

Andrew B. Holmes
_____
NAME

6th June, 2003
_____
DATE